

**FINAL REPORT—BERKELEY PIT INNOVATIVE
TECHNOLOGIES PROJECTS: PURITY SYSTEMS,
INC., AND THE UNIVERSITY OF MONTANA
DEMONSTRATION**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 7**

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Prepared for

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IAG No. DW89935117-01-0

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U.S. Department of Energy
Federal Energy Technology Center
Pittsburgh, Pennsylvania 15236
Contract No. DE-AC22-96EW96405

March 1997

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March 1997

Final Report—Berkeley Pit Innovative Technologies Projects: Purity Systems, Inc., and the University of Montana Demonstration

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Foreword

Today industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources, and under a mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define, measure the impacts, and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the Department of Energy (DOE) has responsibilities similar to the NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc. (MSE), and Montana Tech of The University of Montana for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communication link between the researcher and the user community.

The objective of this demonstration was to show that silica gel/polymer composite materials, developed by Purity Systems, Inc., in Missoula, Montana, could be used to precipitate out the iron and aluminum in the Berkeley Pit water and to separate the copper, zinc, and manganese present in the water. In addition, these metals could be quantitatively recovered from the composite materials in a pure and more concentrated form than what is currently present in the untreated water.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by either the EPA or DOE.

Executive Summary

The Berkeley Pit located in Butte, Montana, is an inactive open-pit copper mine designated by the Environmental Protection Agency (EPA) as one of the nation's largest Superfund sites. Presently, the Pit contains more than 25 billion gallons of highly acidic and metal ion-enriched water. The Pit has been filling at a rate of 5 to 7.6 million gallons per day since 1982 when operations ceased at the Pit. The Berkeley Pit not only poses a serious environmental hazard but also provides an excellent business opportunity for extracting valuable metals.

Aluminum (Al), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) exist in the Berkeley Pit water at concentrations ranging from 215 parts per million (ppm) for Cu to 1,112 ppm for Fe. Among the five metal ions, only Cu, Mn, and Zn are referred to as valuable metals. To obtain a value of each metal ion, the metal ion must be pure and exist at a high concentration (3 to 5%).

The goal of this bench-scale demonstration was to precipitate out the Fe and Al with a base and subsequently speciate and concentrate the Cu, Mn, and Zn.

The precipitation process was developed originally by Dr. Huang from Montana Tech of The University of Montana (Montana Tech) and was modified to suit the needs of the demonstration.

The speciation process was achieved by using three types of chelator silica gel developed by Purity Systems, Inc., of Missoula, Montana. The chelator was covalently bonded to the silica gel through a primary coating that was also covalently bonded to the silica gel to ensure much greater resistance toward acid and base extremes during the operation. With this innovative chemistry, the gel can be reused for thousands of cycles and subsequently warrants the feasibility of using the chelator gel for resource recovery.

The bench-scale demonstration performed at Montana Tech during March 1996 successfully displayed the recovery of high purity and high concentration of Cu, Mn, and Zn.

A pilot-scale demonstration would provide more detailed information and perimeters toward full-scale production.

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1. INTRODUCTION

The controversial and challenging process of remediating the Berkeley Pit water in Butte, Montana, would be facilitated if metals, such as copper (Cu), manganese (Mn), and zinc (Zn), could be removed in a pure and concentrated form suitable for commercial use. The money generated from recovering these metals could offset the cost of the remediation process, therefore, making remediation a feasible alternative.

materials in a pure and more concentrated form

A technology recently developed at Purity Systems, Inc., in Missoula, Montana, offers the possibility of separating these metal ions from the water using a series of regenerable materials that show selective binding even in the presence of high concentrations of Calcium (Ca^{+2}). For this technology to work properly, the large amounts of iron (Fe) and aluminum (Al) found in Berkeley Pit water must first be removed without significantly disturbing the concentrations of the more useful metals. Testing has proven that by adding hydrogen peroxide (H_2O_2) to Berkeley Pit water followed by adjusting the pH of the water to 4.7 results in complete precipitation of iron (as Fe^{+3}). In addition, the same tests also precipitated a majority of the Al while leaving the concentration of Cu at 75% of its original concentration and leaving Zn and Mn concentrations unchanged. The percentage of Cu retained in solution was found to be sensitive to pH with changes of 0.1 pH unit producing changes in percent Cu from 10 to 15 percent. This treatment uses much less base than previous precipitation protocols and is more selective.

The goal of this demonstration was to show that the silica gel/polymer composite materials, developed by Purity Systems, Inc., could be used to separate Cu, Zn, and Mn from Berkeley Pit water. In addition, these metals could be quantitatively recovered from the composite

than what is currently present in the untreated water.

Three related materials (WP-1, WP-2, and WP-3) used in the demonstration, which differ only by their affinity for given types of metal ions, were developed by Purity Systems, Inc., at the University of Montana as part of a developmental process that began in 1993. During the demonstration, each material was employed in three small columns in series to effect speciation of the metals of concern. The captured metals were then released from each individual column by acid elution. The column flow-through and the eluted metal concentrates were then analyzed by inductively coupled plasma (ICP) methods for metal concentration.

The results obtained indicate the feasibility of using the three demonstration materials and protocols for remediating Berkeley Pit water. Further optimization and scaleup of these processes is warranted, as indicated throughout this report.

The Berkeley Pit water demonstration was performed in the Mine Waste Technology Program (MWTP) laboratories at Montana Tech of The University of Montana (Montana Tech) in Butte, Montana. The equipment and Berkeley Pit water samples for the demonstration were provided by the Environmental Protection Agency (EPA)-sponsored MWTP. Mr. Henry Bogert of Montana Tech organized the demonstration. Mr. David Pang of Purity Systems, Inc., performed the demonstration and collaborated with Professor Edward Rosenberg of the University of Montana in developing the demonstration protocol. The ICP analyses were performed by Mr. Wayne Svec of Montana Tech according to EPA protocols. Ms. Catherine Wassmann of Montana Tech assisted in setting up the demonstration.

2. PROCESS DESCRIPTION

The Berkeley Pit has a high concentration of Fe^{+2} . Therefore, the water was treated with H_2O_2 to oxidize Fe^{+2} to Fe^{+3} and to allow for Fe to later be removed by precipitation. Following oxidation, the pH of Pit water was increased by adding a solution of sodium hydroxide (NaOH), which resulted in the removal of most of the Al and Fe by precipitation. The goal of this step, which was achieved, was to adjust the pH of the water so the supernatant concentration of Al and Fe was low and the concentration of Cu, Mn, and Zn was largely unchanged.

Following the addition of NaOH, a preliminary evaluation of the Berkeley Pit water indicated a pH end point of between 4.4 and 5; therefore, a series of zero-in pH adjustment tests were needed to find the exact pH end point. Once the

pH end point was determined, the pretreatment protocol was established. This protocol can be used to treat larger quantities of Berkeley Pit water. The resulting supernatant, laden with high concentrations of Cu, Mn, and Zn, was used for the speciation demonstration.

In this speciation demonstration test, three chelator materials, labeled WP-1, WP-2, and WP-3, were evaluated.

Three plastic columns, each containing the same amount of WP-1, were connected in series. The pretreated Berkeley Pit water was pumped continuously through these three columns by a valveless mechanical pump at a flow rate of 50 milliliters per minute (mL/min).

Three speciation cycles were performed on the WP-1 columns (see Figure 2-1).

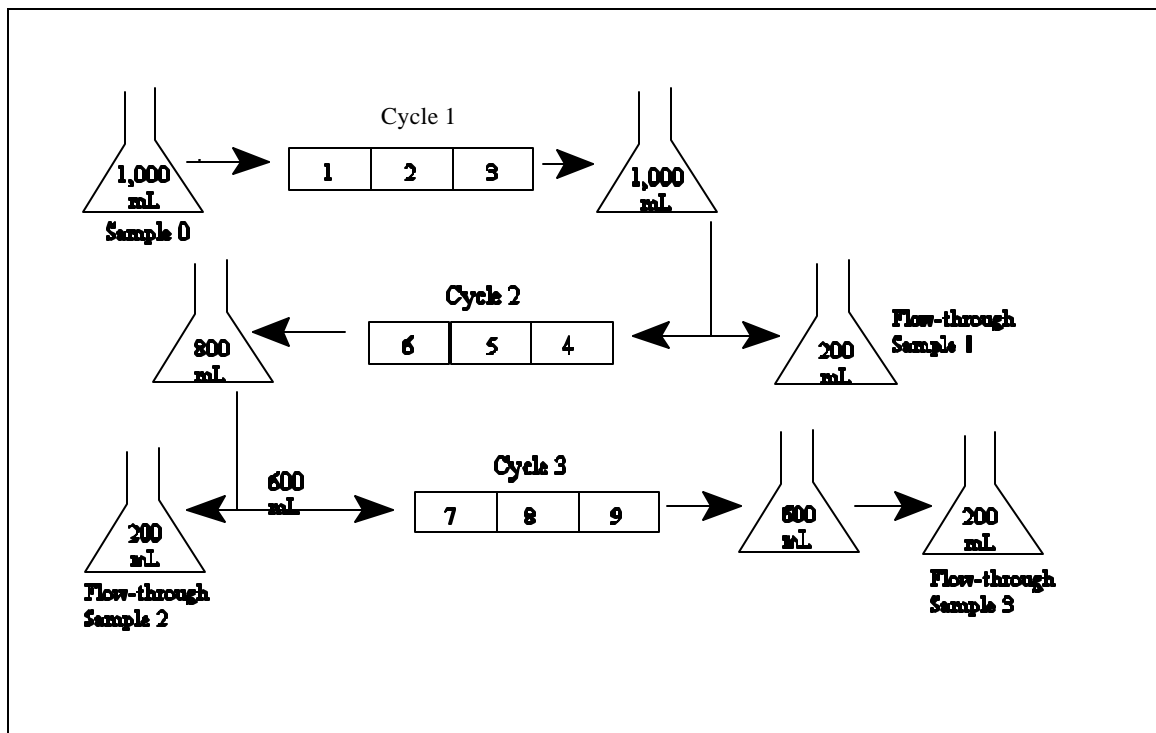


Figure 2-1. Scheme of speciation test.

Cycle 1: A specified amount of the pretreated Berkeley Pit water was pumped through the three columns. After collecting a fixed amount of flow-through the columns were disassembled and the bound metal ions from each of the three columns were eluted with hydrochloric acid (HCl). The acid eluate from each of the three columns was collected individually in labeled plastic containers. A fraction of the flow-through water was also collected in a labeled plastic container and preserved with concentrated nitric acid (HNO₃). The three columns were then reconnected, the excess acid remaining in the three columns was pumped out with deionized (DI) water, and the metal binding capacity was regenerated with ammonium hydroxide (NH₄OH). The excess NH₄OH was removed with DI water, and the columns were then ready for the second cycle.

Cycle 2: The remaining flow-through water from the first cycle was pumped through the three columns, and the flow-through was collected. After pumping all the water through the columns, the three columns were disassembled, and the bound metal ions were eluted and

collected as in the first cycle. A fraction of the flow-through water was also collected and preserved, and the columns were reconnected and regenerated as in the first cycle.

Cycle 3: The remaining flow-through water from the second cycle was pumped through the columns, and the flow-through was collected. After pumping the water through the columns, the three columns were disassembled, and the bound metal ions were eluted and collected as in the second cycle. A fraction of the flow-through water was also collected and preserved as in the second cycle.

After regenerating the columns, the above three cycles were repeated with the same columns and protocol but only at a 25 mL/min flow rate.

After the speciation tests for WP-1 were completed, the speciation demonstration was repeated using both WP-2 and WP-3 chelator gel.

The metal ion profile in all the samples collected was determined by ICP according to the EPA-specified procedures to ensure the validity of the resulting values.

3. DEMONSTRATION TEST PROCEDURE

Based on the concentration of the Fe^{+2} in the Berkeley Pit water, 1.1 mL of 30% H_2O_2 was sufficient to oxidize all the Fe^{+2} in 500 mL of Berkeley Pit water to Fe^{+3} (as seen in the calculation of the required H_2O_2 below). This amount of H_2O_2 was used or scaled up proportionately to treat the original Berkeley Pit water, depending on the quantity tested.

$(W \cdot F \cdot 1.05) / (A \cdot P \cdot D) = \text{volume (mL) of 30\% } \text{H}_2\text{O}_2 \text{ needed for 500 mL of Berkeley Pit water.}$

where...

W = weight (in grams) of Fe^{+2} in 500 mL of Berkeley Pit water.

F = formula weight of H_2O_2 .
1.05 = 5% excess.

A = atomic weight of Fe.

P = percent concentration of H_2O_2 solution.

D = density of 30% H_2O_2 solution.

A series of pH titration tests were performed with 500 mL each of Berkeley Pit water.

3.1 pH End-Point Determination

A graduated cylinder was used to measure out 500 mL of Berkeley Pit water, and the water was then poured into a 500-mL Erlenmeyer flask. A magnetic stir bar was placed into the flask, and the flask was put on a magnetic stirrer. A pH probe and a thermometer were immersed into the water, and the original pH and temperature of the water were measured and recorded. The temperature of treated Berkeley Pit water, which ranged between 22 to 24 EC throughout the demonstration, had no significant effect on pH.

While stirring, 1.1 mL of 30% H_2O_2 were added using a dropper. After stirring for 10 minutes, 2.5 normal (N) NaOH solution was added with a

dropper to adjust the pH of the water to 4.4; the amount of NaOH solution used was recorded. This procedure was repeated three additional times, each with 500 mL of the oxidized Berkeley Pit water and with the pH of the water titrated to 4.6, 4.8, and 5.0, respectively. After settling for 24 hours, 200 mL of the supernatant from each of the four flasks was filtered, collected in four labeled plastic containers, and measured to determine a pH level. No significant pH variation was observed after the 24-hour settling period. After the pH measurement, 2.0 mL of concentrated HNO_3 were added to each container to preserve the samples, and the metal ion profile of each sample was determined by ICP.

After evaluating the pH adjustment results, it was determined that for every 500 mL of oxidized Berkeley Pit water, 13.5 mL of 2.5 N of NaOH were needed to adjust the pH of the water. The pH was adjusted to a point where the concentrations of Fe and Al were low, and concentrations of Mn, Zn, and especially Cu were still quite high. Data is given in Section 4.

3.2 Preparation of Stock Pit Water for Speciation

A 5-gallon plastic container was calibrated and scaled with liter 1 (L) graduations and filled with 16 L of Berkeley Pit water. A mechanical stirrer and a pH probe were immersed into the water. While stirring, 35.2 mL of 30% H_2O_2 were added over a 10-minute period. Once the H_2O_2 was added, the solution was stirred for 30 additional minutes. After the 30 minutes, 432 mL of 2.5 N NaOH solution were added using a dropper over a 40-minute period; the mixture was then stirred for 2 hours. The container was covered (not sealed to avoid pressure buildup) and was stored at room temperature for 24 hours.

After settling for 24 hours, 7 L of the supernatant

were filtered through fine filter paper, and the filtrate was collected in a 7.5-L, small-mouth plastic container for the speciation demonstration. (This filtrate is hereon referred to as the control water.)

Two-hundred mL of this water were collected in a 250-mL plastic container, and 2 mL of concentrated HNO_3 were added to preserve the sample. The metal profile of this water sample was used as the initial input profile for the speciation test.

3.3 Speciation Demonstration

A schematic sequence of the speciation demonstration is shown in Figure 2-1.

3.3.1 Speciation Test with WP-1 at 50 mL/min Flow Rate

Three plastic containers (1.0 x 4.5 centimeter (cm)), each packed with 2.0 grams (g) of WP-1 chelator gel, were connected in series.

Cycle 1: The control water was pumped through the three columns at 50 mL/min flow rate. After collecting 1,000 mL of flow-through in a 1-L graduated cylinder, the pump was stopped. Two-hundred mL of this flow-through (FT-1) were collected in a 250-mL labeled plastic container, and 2 mL of concentrated HNO_3 were added to preserve the water for ICP analysis. The metal profile in this flow-through sample provides information of the metal ion removal from the control water in Cycle 1.

The columns were washed by pumping 30 mL of DI water through the columns to remove residual input water. The three columns were then disconnected, and the bound metal ions from each column were eluted with 20 mL of 1 N

HCl and collected in three labeled plastic containers. After eluting the bound metal ions from each column, the three columns were reconnected, and the excess acid was removed by pumping 75 mL of DI water through the columns. The metal-capturing capability of the columns was regenerated by pumping 30 mL of 1 N NH_4OH through the columns followed by pumping 75 mL of DI water to remove residual NH_4OH remaining in the columns.

Cycle 2: The 800 mL of flow-through water from Cycle 1 were pumped through the three regenerated columns at a 50 mL/min flow rate. After collecting 800 mL of flow-through water in a 1-L graduated cylinder, 200 mL of this flow-through (FT-2) were collected in a 250-mL labeled plastic container, and 2 mL of concentrated nitric acid were added to preserve the water for ICP analysis. The metal profile in this flow-through sample provides information for the metal ion removal from the control water in Cycle 2.

The metal-laden columns were washed by pumping 30 mL of DI water through the columns to remove residual input water. The three columns were then disconnected, and the bound metal ions from each column were eluted with 20 mL of 1 N HCl and were collected in three labeled plastic containers. After eluting the metal ions from these columns, the three columns were reconnected, and the excess acid was removed by pumping 75 mL of DI water through the columns. The columns were regenerated by pumping 30 mL of 1 N NH_4OH through the columns followed by 75 mL of DI water.

Cycle 3: The 600 mL of flow-through water from Cycle 2 were pumped through the three regenerated columns at a flow rate of 50 mL/min. After collecting 600 mL of flow-through in a 1-L graduated cylinder, 200 mL of this flow-through (FT-3) were collected in a 250-mL labeled plastic container, and 2 mL of concentrated HNO₃ were added to preserve the water for ICP analysis. The metal profile in this flow-through sample provides information on the metal ion removal from control water in Cycle 3.

The metal ion-laden columns were washed by pumping 30 mL of DI water through the columns. The columns were then disconnected, and the bound metal ions from each column were eluted with 20 mL of 1 N HCl and collected in three labeled plastic containers. At the end of this test, nine metal ion-concentrated water samples and three flow-through samples were ready for ICP analysis.

3.3.2 Speciation Test with WP-1 at 25 mL/min Flow Rate

This test follows the precise procedures described in Section 3.3.1 with the exception of the pumping rate, which was changed to 25 mL/min.

3.3.3 Speciation Test with WP-2 at 50 mL/min Flow Rate

This test follows the precise procedures described in Section 3.3.1 with the exception of the chelator gel, which was changed to WP-2.

3.3.4 Speciation Test with WP-2 at 25 mL/min Flow Rate

This test follows the precise procedures described in Section 3.3.2 with the exception of the chelator gel, which was changed to WP-2.

3.3.5 Speciation Test with WP-3 at 50 mL/min Flow Rate

This test follows the precise procedures described in Section 3.3.1 with the exception of the chelator gel, which was changed to WP-3.

3.3.6 Speciation Test with WP-3 at 25 mL/min Flow Rate

This test follows the precise procedures described in Section 3.3.2 with the exception of the chelator gel, which was changed to WP-3.

At the conclusion of the speciation demonstration, 54 metal ion-concentration samples, 18 flow-through samples, and 1 control water sample were ready for ICP analysis.

4. DEMONSTRATION TEST RESULTS

The pH end-point determination results are shown in Table 4-1.

Based on the results from Table 4-1, a ratio of 13.5 mL to 2.5 N NaOH added to 500 mL oxidized Berkeley Pit water was used to prepare 16 L of water for the speciation test. The average Fe^{+3} concentration in the influent water was less than 1 parts per million (ppm), and Fe^{+2} was approximately 3 ppm (see Appendix A).

4.1 Speciation Test with Wp-1 at 50 mL/min Flow Rate

The metal ion concentrations of the nine metal ion concentrated samples (three samples from each cycle) obtained using WP-1 chelator gel operated at 50 mL/min flow rate are shown in Table 4-2 and depicted in Figure 4-1. The relative percent concentration of each metal ion in each sample is tabulated and shown in Table 4-3. The calculation of the relative percent concentration was based on: $M / (M + \text{Al} + \text{Cu} + \text{Mn} + \text{Zn})$ (mg/L) / (Al + Cu + Mn + Zn) (mg/L). The concentrations of potassium (K), sodium (Na), and silicon (Si) were not included in these calculations [the quality assurance project plan per (QAPP)]. All other heavy metal ion concentrations were in the range of 0 to 10 ppm and had no significant impact on the reported percentage purity for the concentrated metal ions. Thus, inclusion of all other heavy metal ions changes the percentage of Cu purity by less than 1%, which is similar to Mn and Zn (see Appendix A). The metal ion concentration of the control water and the three flow-through water samples are shown in Table 4-4 and in Figure 4-2.

Table 4-2, Figure 4-1, and Table 4-3 indicate that WP-1 has a very high affinity toward Al and Cu ions since samples 1, 2, and 3 show high concentrations of both Al and Cu. As the Al and

Cu ions were depleted, the WP-1 started to use capturing capability to bind Zn as shown in samples 4, 5, 6, 7, and 8 in which high Zn concentration is observed. After all the Zn ions were removed, the gel started to bind Mn ion as observed in sample 9.

The flow-through water metal ion profiles shown in Figure 4-2 and Table 4-4 indicate that, compared to the control water sample 0, sample 1 has a very low concentration of Al and Cu with little change of the concentration of Zn and Mn. In sample 2, since most of the Al and Cu have been removed, the Zn concentration decreased significantly with the Mn concentration remaining the same. In sample 3, the remaining Zn and some of the Mn are removed. These results complement the metal ion concentrate profile, demonstrating excellent recovery as well as capture and speciation.

4.2 Speciation Test with Wp-1 at 25 mL/min Flow Rate

The metal ion profiles of the nine metal ion concentrated samples are shown in Table 4-5 and depicted in Figure 4-3. Percent concentration of each metal ion is shown in Table 4-6. The metal ion profile of the flow-through water is shown in Table 4-7 and depicted in Figure 4-4.

The purpose of the 25 mL/min flow rate test was to demonstrate that the speciation capability of WP-1 will not change if the loading flow rate is changed. Comparing Tables 4-2 and 4-5, Tables 4-3 and 4-6, and Tables 4-4 and 4-7 and Figures 4-1 and 4-3 and Figures 4-2 and 4-4, it is evident the speciation results are similar for the two operational flow rates tested. These results warrant trying even faster flow rates.

4.3 Speciation Test with Wp-2 at 50 mL/min Flow Rate

The metal ion profiles of the nine metal concentration samples with WP-2 at a flow rate of 50 mL/min are shown in Table 4-8 and depicted in Figure 4-5. The percent concentrations are shown in Table 4-9. The metal ion profile of the flow-through water is shown in Table 4-10 and depicted in Figure 4-6.

The speciation test with WP-2 at 50 mL/min shows that the gel has a higher affinity toward Cu versus Al compared to WP-1. Tables 4-8 and 4-9 and Figure 4-5 show that samples 1 and 2 have very high concentrations of Cu only. After Cu is removed, the gel starts to capture Zn, as indicated with sample 3.

Purity Zn was obtained from samples 4 through 9. The overall capacity of WP-2 was not as high as WP-1. In addition, Al existed in all nine of the samples at concentrations varying from 1.8 to 6.8%. Minimal amounts of Mn were captured compared to WP-1. The metal ion profile in the flow-through water samples also matched the results from the nine concentrated samples. For example, in comparing Figures 4-5 and 4-6, the metal ion profiles were complementary with respect to the flow-through metal ion concentrations. Thus, sample 1 in Figure 4-6 contains no Cu while samples 1 through 3 in Figure 4-5 contain almost all Cu. A similar scenario pertains to the other metals as well. Table 4-10 and Figure 4-8 indicate the Cu in sample 1 was almost completely removed, that a considerable amount of Al still remained in the flow-through water, and that Zn and Mn concentrations were nearly unchanged. In sample 2, some Al remained, and the Zn concentration was reduced significantly. The Mn concentration remained the same as in the control sample 0. Sample 3 still had some Al left. The Zn concentration was further reduced in sample 3, and none of the Mn was removed.

4.4 Speciation Test with WP-2 at 25 mL/min

Flow Rate

The concentrated metal ion profile from the speciation test with WP-2 at a flow rate of 25 mL/min is shown in Table 4-11 and depicted in Figure 4-7. The percent concentration of each metal ion is shown in Table 4-12. The metal ion profile of the flow-through water is shown in Table 4-13 and depicted in Figure 9.

As in the WP-1 test, the goal of the speciation test using WP-2 at a reduced (25 mL/min) flow rate was to investigate the relationship between flow rate and capture kinetics. By comparing the results from Tables 4-8 and 4-11, Tables 4-9 and 4-12, and Tables 4-10 and 4-13 and Figures 4-6 and 4-7 and Figures 4-6 and 4-8, it is determined that changing the flow rate from 25 mL/min to 50 mL/min had no effect on the metal speciation performance of WP-2.

4.5 Speciation Test with WP-3 at 50 mL/min Flow Rate

The last chelator gel used in the speciation test was WP-3. The test was performed at a flow rate of 50 mL/min. The concentrated metal ion profile from the speciation test using WP-3 at a flow rate of 50 mL/min is shown in Table 4-14 and in Figure 4-9. The percent concentration of the metal ions in the concentration samples is shown in Table 4-15. The metal ion profile of the flow-through water is shown in Table 4-16 and depicted in Figure 4-10.

Tables 4-14 and 4-15 and Figure 4-9 indicate that WP-3 binds Al and Cu effectively and performs similarly to WP-1. These results are realized by comparing samples 1, 2, and 3 from Tables 4-14 and 4-15 and Figure 9 with the same samples in Tables 4-2 and 4-3 and Figure 4-1. Samples 4 through 9 contain high concentrations of Zn, which is also similar to WP-1, except that each sample (sample 4 through 9) still has significant concentrations of Cu in the case of WP-3. The flow-through water metal profile shown in Table

4-16 and Figure 4-10 agree with these results. For example, in comparing Figures 4-9 and 4-10, sample 1 in Figure 4-10 contains no Al or Cu and indicates a reduction of Zn, while samples 1 through 3 in Figure 4-9 contain almost all the Al and Cu and some Zn. Samples 1, 2, and 3 of the flow-through water have a very low concentration of Al and Cu. The Zn concentration decreased as it was removed by WP-3. Manganese does not show any significant binding to WP-3. The residual Cu in concentrated samples 1 through 9 could be attributed to inefficient elution of the Cu from the columns.

concentrated samples is shown in Table 4-17 and in Figure 4-11. The percent concentration of the concentrated metal ion is shown in Table 4-18. The metal ion profile of the flow-through water is shown in Table 4-19 and in Figure 4-12.

Once again, the speciation test was run at a flow rate of 25 mL/min with WP-3 showing similar results when compared to the 50 mL/min flow rate.

4.6 Speciation Test with WP-3 at 25 mL/min Flow Rate

The metal ion concentration profile of the

Table 4- 1. pH end-point determinations.

pH	NaOH (mL)	Al (ppm*)	Cu (ppm*)	Fe (ppm*)	Mn (ppm*)	Zn (ppm*)
BP** water	0	275.3	179	1137.4	208.6	580.5
4.4	8.8	195.1	162.6	2.2	198.3	561.3
4.6	11.6	88.8	153	0.5	207.7	598.8
4.8	13.5	27.9	102.3	0.5	203	585.5
5	14	18.8	71.7	0.1	205.3	561.3
* ppm - parts per million						
**BP - Berkeley Pit						

Table 4-2. Metal ion concentration profile (ppm).

	Al	Cu	Mn	Zn
1	672.1	2,632.5	11.9	115.4
2	531.1	2,369.1	37.4	253.1
3	434.0	1,128.6	28.2	1,355.9
4	44.8	12.5	41.8	2,718.4
5	10.5	4.5	114.5	2,769.7
6	12.9	3.1	157.0	2,772.0
7	4.9	0.6	100.3	2,773.2
8	3.1	0.5	239.3	2,774.0
9	1.4	0.3	764.5	1,273.0

Table 4-3. Relative percent (%) concentration of metal ion.

	Al	Cu	Mn	Zn
0	4.4%	14.1%	22.9%	58.6%

1	19.6%	76.7%	0.3%	3.4%
2	16.6%	74.3%	1.2%	7.9%
3	14.7%	38.3%	1.0%	46.0%
4	1.6%	0.4%	1.5%	96.5%
5	0.4%	0.2%	3.9%	95.5%
6	0.4%	0.1%	5.3%	94.1%
7	0.2%	0.0%	3.5%	96.3%
8	0.1%	0.0%	7.9%	91.9%
9	0.1%	0.0%	37.5%	62.4%

Table 4-4. Metal ion profile of flow-through water (ppm).

	pH	Al	Cu	Mn	Zn
0	4.70	41.1	131.9	214.3	548.6
1	6.30	1.9	0.1	193.0	503.9
2	6.60	0.9	0.0	193.0	257.2
3	8.60	0.8	0.0	153.0	3.5

Table 4-5. Metal ion concentration profile (ppm).

	Al	Cu	Mn	Zn
1	702.1	2,668.9	30.0	100.6
2	548.7	2,371.9	61.2	160.7
3	368.4	929.7	83.2	1,401.5
4	18.1	16.2	112.2	2,776.2
5	12.4	5.2	166.3	2,769.7
6	11.0	2.4	190.0	2,771.3
7	4.8	0.8	194.4	2,772.3
8	6.2	1.3	248.2	2,371.4
9	4.6	0.1	696.8	1,472.5

Table 4-6. Relative percent (%) concentration of metal ion.

	Al	Cu	Mn	Zn
0	4.4%	14.1%	22.9%	58.6%
1	20.1%	76.2%	0.9%	2.9%
2	17.5%	75.5%	1.9%	5.1%
3	13.2%	33.4%	3.0%	50.4%
4	0.6%	0.6%	3.8%	95.0%
5	0.4%	0.2%	5.6%	93.8%
6	0.4%	0.1%	6.4%	93.2%

7	0.2%	0.0%	6.5%	93.3%
8	0.2%	0.0%	9.4%	90.3%
9	0.2%	0.0%	32.1%	67.7%

Table 4-7. Metal ion profile of flow-through water (ppm).

	pH	Al	Cu	Mn	Zn
0	4.70	41.1	131.9	214.3	548.6
1	6.20	0.9	0.0	208.4	534.9
2	6.60	0.4	0.0	190.6	263.2
3	8.64	0.5	0.0	142.6	1.4

Table 4-8. Metal ion concentration profile (ppm).

	Al	Cu	Mn	Zn
1	48.1	2,451.5	4.7	109.9
2	47.1	2,213.2	5.7	215.8
3	86.8	1,193.5	8.9	820.7
4	112.4	139.8	8.0	1,396.5
5	99.0	79.2	10.7	1,586.2
6	89.2	52.2	11.8	1,594.0
7	86.8	14.5	11.7	1,438.9
8	71.4	11.9	16.1	1,508.6
9	78.3	10.0	24.1	1,680.1

Table 4-9. Relative percent (%) concentration of metal ion.

	Al	Cu	Mn	Zn
0	4.4%	14.1%	22.9%	58.6%
1	1.8%	93.8%	0.2%	4.2%
2	1.9%	89.2%	0.2%	8.7%
3	4.1%	56.6%	0.4%	38.9%
4	6.8%	8.4%	0.5%	84.3%
5	5.6%	4.5%	0.6%	89.4%
6	5.1%	3.0%	0.7%	91.2%
7	5.6%	0.9%	0.8%	92.7%
8	4.4%	0.7%	1.0%	93.8%
9	4.4%	0.6%	1.3%	93.7%

Table 4-10. Metal ion profile of flow-through water (ppm).

	pH	Al	Cu	Mn	Zn
0	4.70	41.1	131.9	214.3	548.6
1	4.75	29.1	1.3	219.8	549.7

2	4.96	19.9	0.0	212.1	387.6
3	5.45	10.8	0.0	209.4	189.7

Table 4-11. Metal ion concentration profile (ppm).

	Al	Cu	Mn	Zn
1	94.4	2,518.8	3.6	101.6
2	51.4	2,422.2	3.1	162.8
3	86.6	1,015.3	5.2	920.5
4	108.8	83.8	4.1	1,303.4
5	89.8	66.8	5.4	1,481.7
6	97.9	49.3	7.7	1,666.1
7	82.0	8.4	6.7	1,359.7
8	60.5	9.8	8.8	1,443.4
9	50.1	7.3	10.8	1,437.8

Table 4-12. Relative percent (%) concentration of metal ion.

	Al	Cu	Mn	Zn
0	4.4%	14.1%	22.9%	58.6%
1	3.5%	92.7%	0.1%	3.7%
2	1.9%	91.8%	0.1%	6.2%
3	4.3%	50.1%	0.3%	45.4%
4	7.3%	5.6%	0.3%	86.9%
5	5.5%	4.1%	0.3%	90.1%
6	5.4%	2.7%	0.4%	91.5%
7	5.6%	0.6%	0.5%	93.3%
8	4.0%	0.6%	0.6%	94.8%
9	3.3%	0.5%	0.7%	95.5%

Table 4-13. Metal ion profile of flow-through water (ppm).

	pH	Al	Cu	Mn	Zn
0	4.70	41.1	131.9	214.3	548.6
1	4.75	27.5	0.3	221.6	545.9
2	4.96	17.1	0.0	214.9	353.1
3	5.45	7.7	0.0	205.0	158.0

Table 4-14. Metal ion concentration profile (ppm).

	Al	Cu	Mn	Zn
1	614.0	2,376.2	10.3	150.0
2	519.2	2,053.5	16.9	289.3
3	458.8	710.5	27.8	1,015.0
4	93.6	272.6	62.4	2,369.9
5	11.7	130.7	50.0	2,591.0
6	11.0	95.3	51.8	2,724.9
7	7.3	177.6	107.3	2,557.7
8	6.0	146.9	90.3	1,987.4
9	4.7	138.8	148.1	2,192.0

Table 4-15. Relative percent (%) concentration of metal ion.

	Al	Cu	Mn	Zn
0	4.4%	14.1%	22.9%	58.6%
1	19.5%	75.4%	0.3%	4.8%
2	18.0%	71.3%	0.6%	10.0%
3	20.7%	32.1%	1.3%	45.9%
4	3.3%	9.7%	2.2%	84.7%
5	0.4%	4.7%	1.8%	93.1%
6	0.4%	3.3%	1.8%	94.5%

7	0.3%	6.2%	3.8%	89.7%
8	0.3%	6.6%	4.0%	89.1%
9	0.2%	5.6%	6.0%	88.3%

Table 4-16. Metal ion profile of flow-through water (ppm).

	pH	Al	Cu	Mn	Zn
0	4.70	41.1	131.9	214.3	548.6
1	6.66	2.6	0.3	214.0	415.9
2	6.88	0.4	0.0	200.0	218.4
3	7.93	0.9	0.0	191.4	15.7

Table 4-17. Metal ion concentration profile (ppm).

	Al	Cu	Mn	Zn
1	762.2	2,508.9	21.7	105.4
2	572.0	2,508.3	54.0	155.9
3	495.8	1,387.4	40.0	959.6
4	29.1	136.1	84.9	2,541.7
5	9.1	120.7	108.3	2,604.0
6	9.0	106.1	68.4	2,431.9
7	5.5	30.3	118.3	2,417.6
8	5.9	48.1	164.8	2,353.8
9	5.8	86.2	251.1	1,949.1

Table 4-18. Relative percent (%) concentration of metal ion.

	Al	Cu	Mn	Zn
0	4.4%	14.1%	22.9%	58.6%
1	22.4%	73.8%	0.6%	3.1%
2	17.4%	76.2%	1.6%	4.7%
3	17.2%	48.1%	1.4%	33.3%
4	1.0%	4.9%	3.0%	91.0%
5	0.3%	4.2%	3.8%	91.6%
6	0.3%	4.1%	2.6%	93.0%
7	0.2%	1.2%	4.6%	94.0%
8	0.2%	1.9%	6.4%	91.5%
9	0.3%	3.8%	11.0%	85.0%

Table 4-19. Metal ion profile of flow-through water (ppm).

	pH	Al	Cu	Mn	Zn
0	4.70	41.1	131.9	214.3	548.6
1	6.50	1.6	0.0	219.1	560.5

2	6.74	0.9	0.0	208.6	304.5
3	8.40	0.7	0.0	175.5	6.1

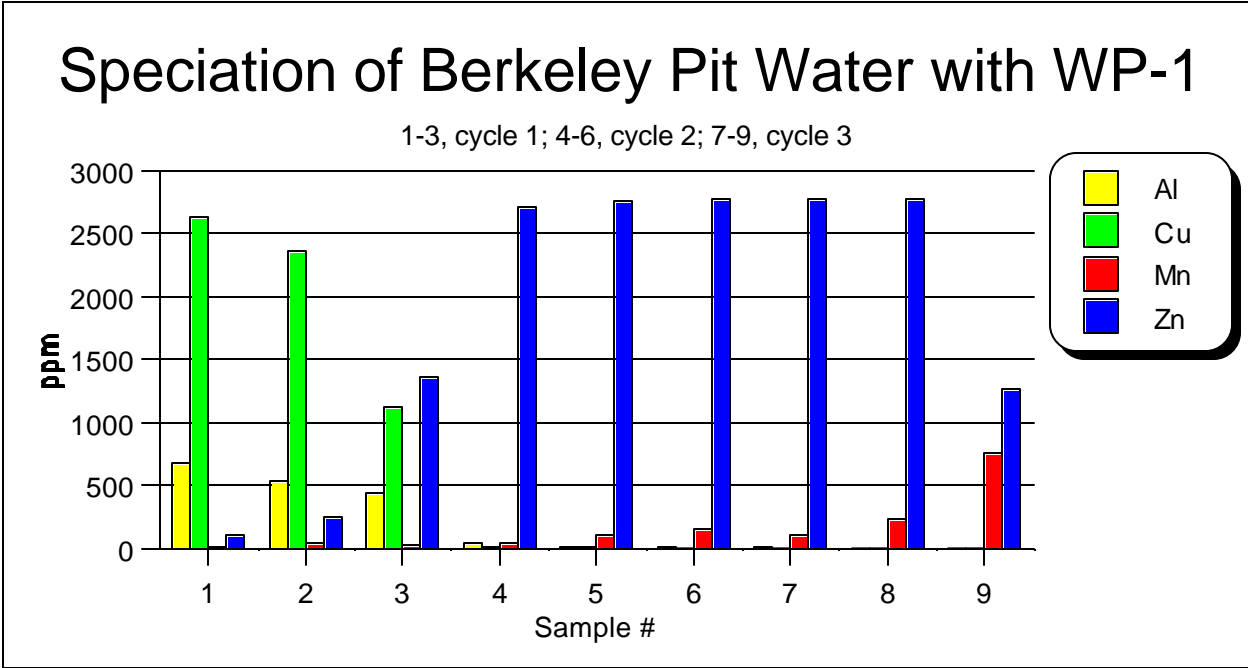


Figure 4-1. Metal ion concentration profile plot.

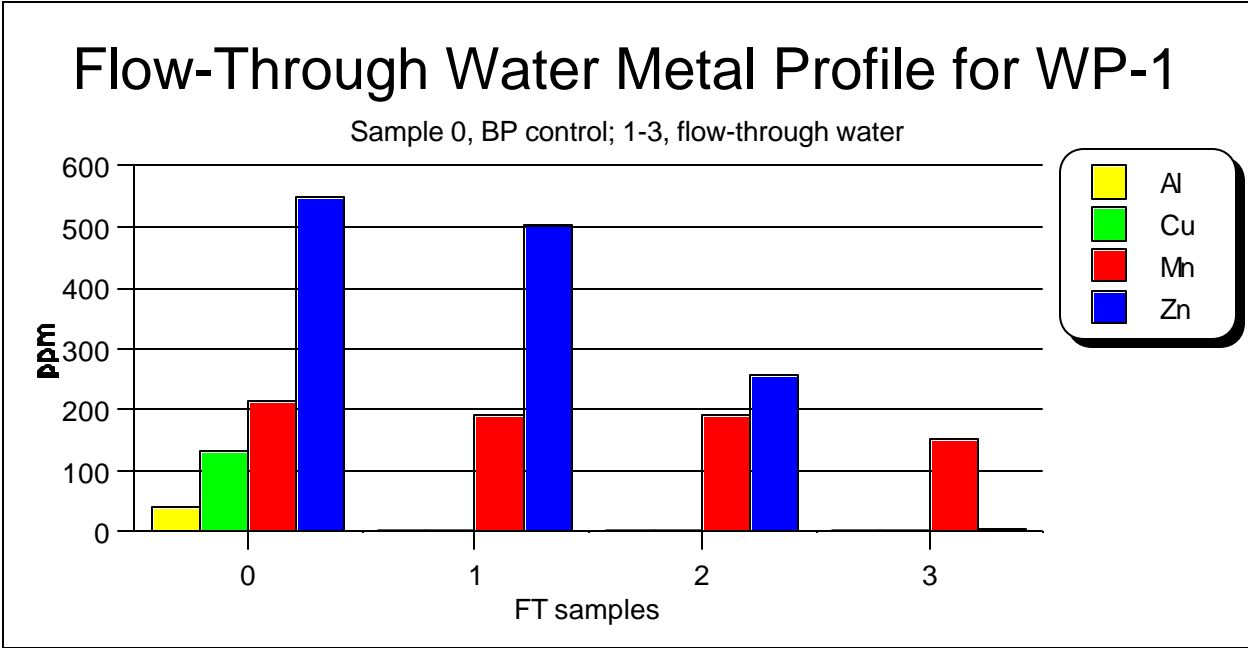


Figure 4-2. Plot of metal ion profile of flow-through water.

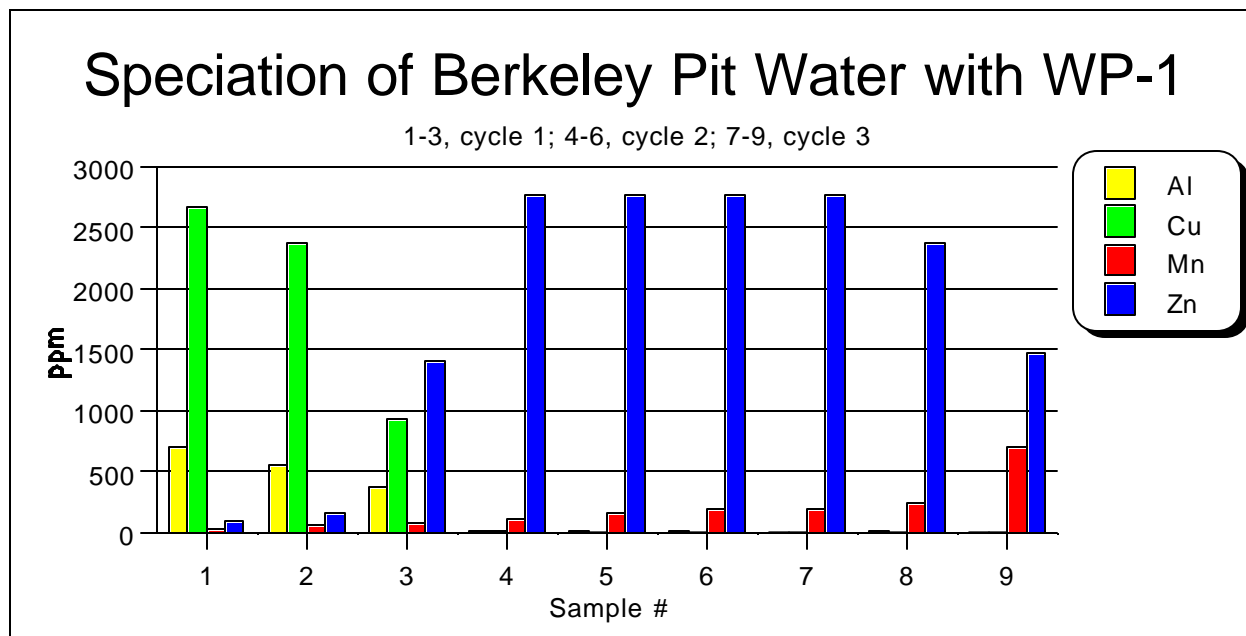


Figure 4-3. Metal ion concentration profile plot.

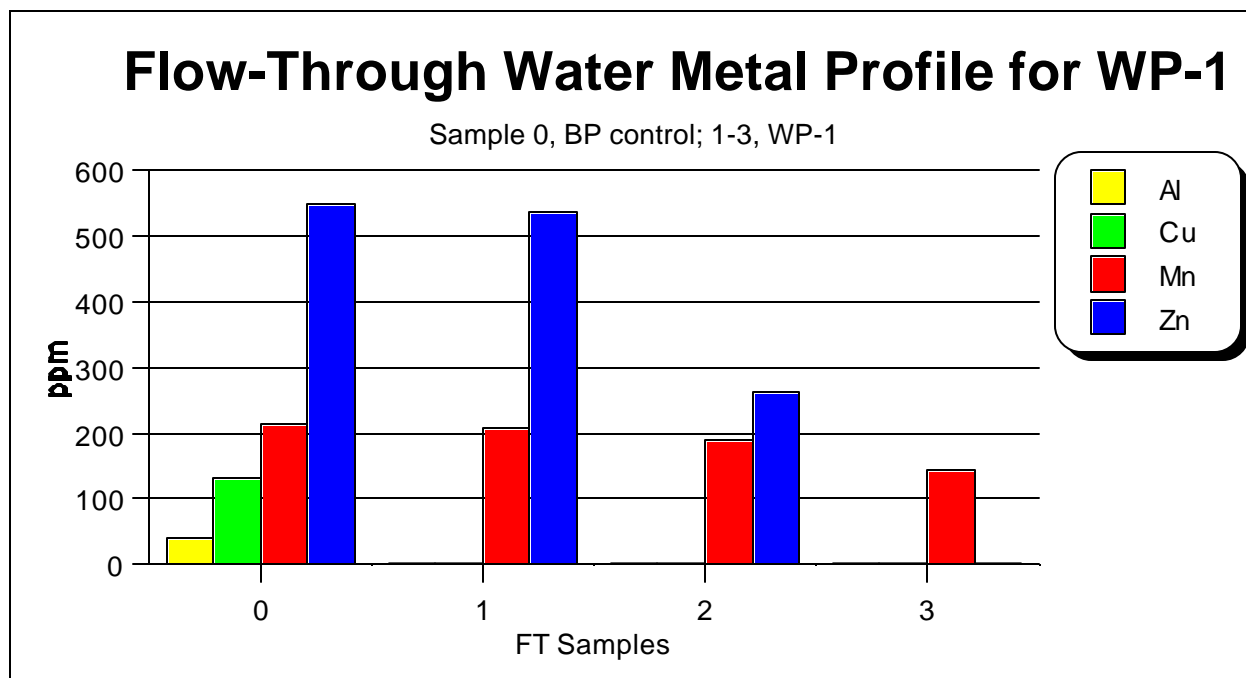


Figure 4-4. Plot of metal ion profile of flow-through water.

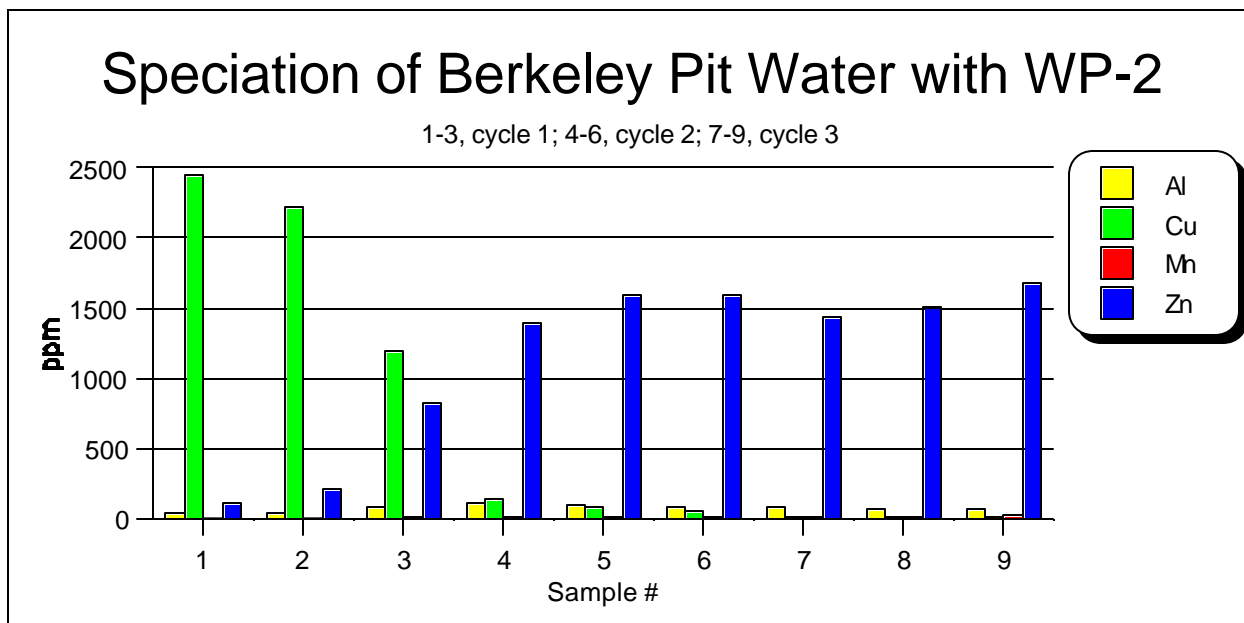


Figure 4-5. Metal ion concentration profile plot.

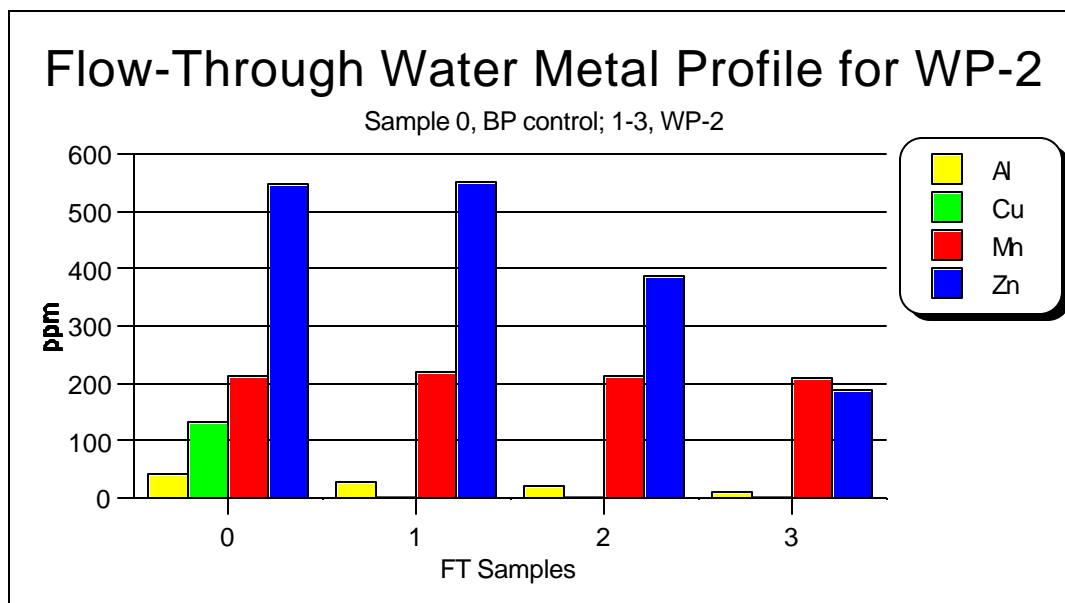


Figure 4-6. Plot of metal profile of flow-through water.

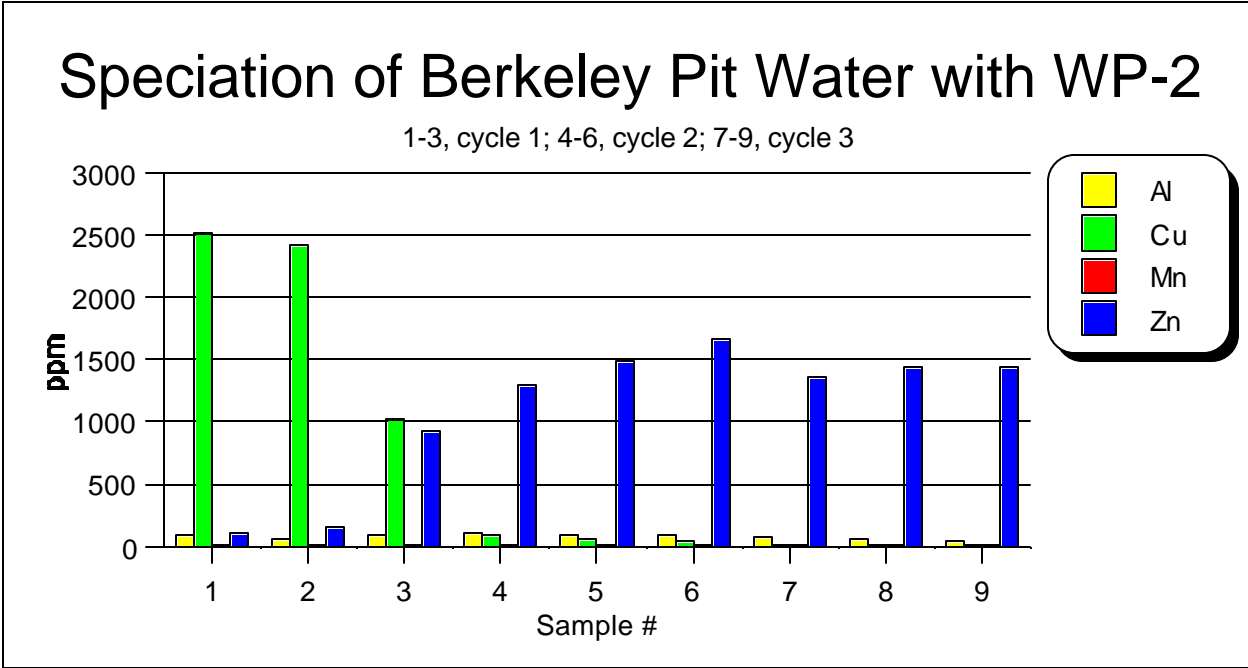


Figure 4-7. Metal ion concentration profile plot.

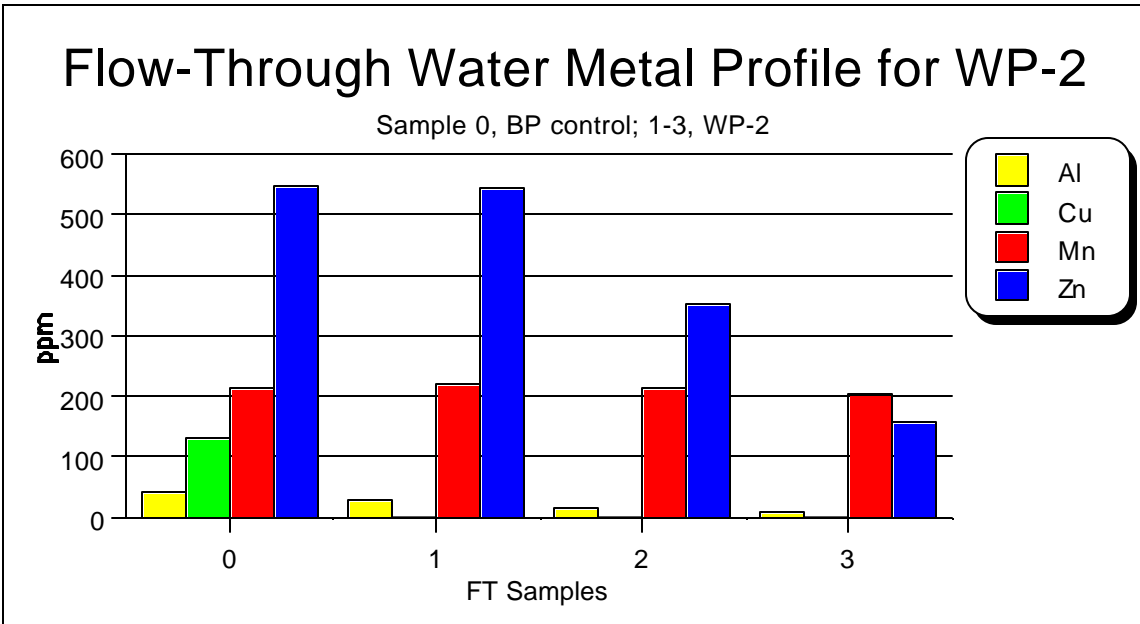


Figure 4-8. Plot of metal ion profile of flow-through water.

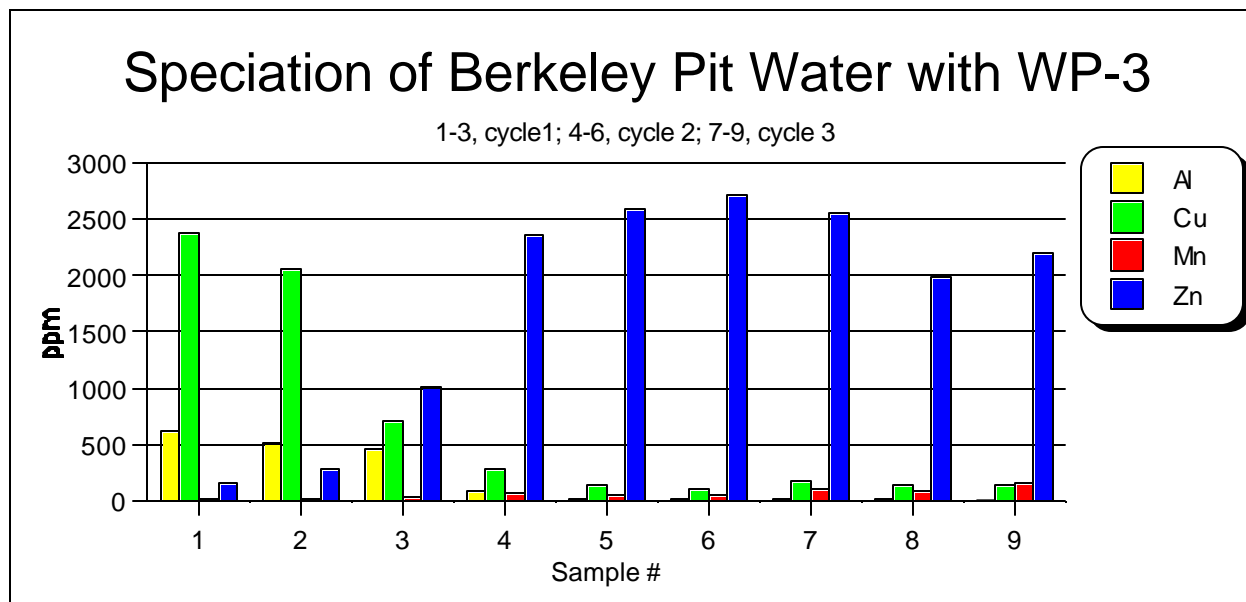


Figure 4-9. Metal ion concentration profile plot.

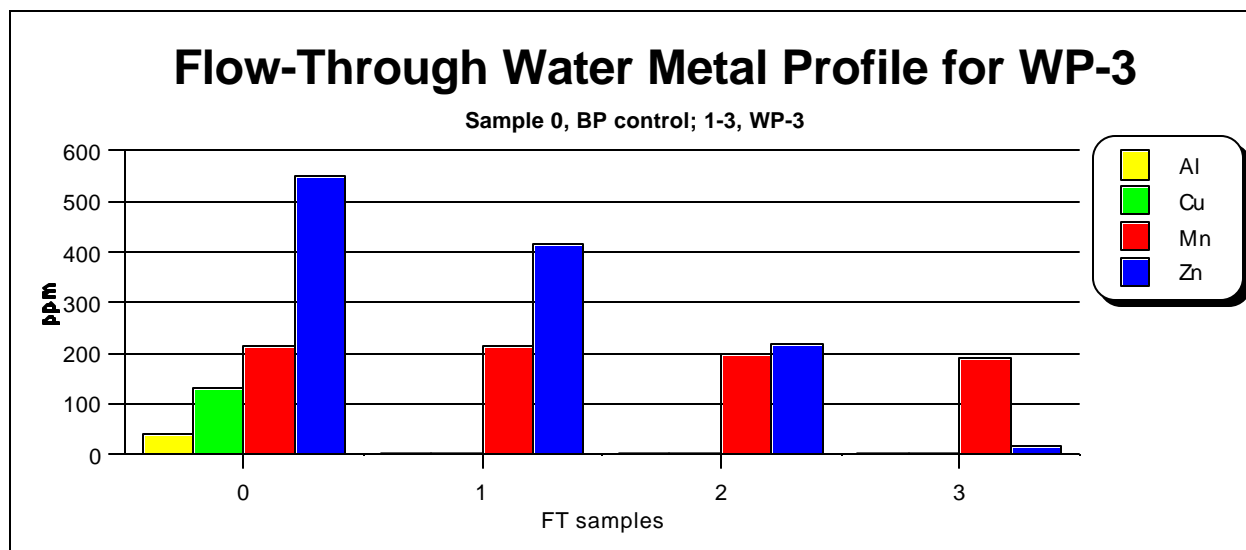


Figure 4-10. Plot of metal ion profile of flow-through water.

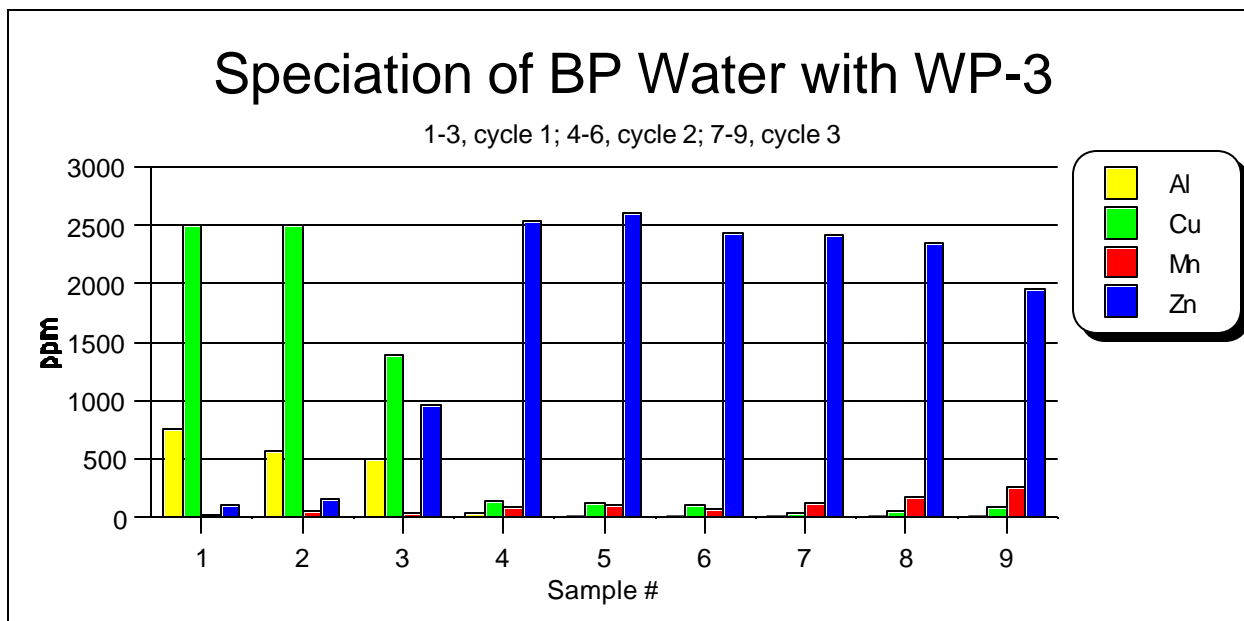


Figure 4-11. Metal ion concentration profile plot.

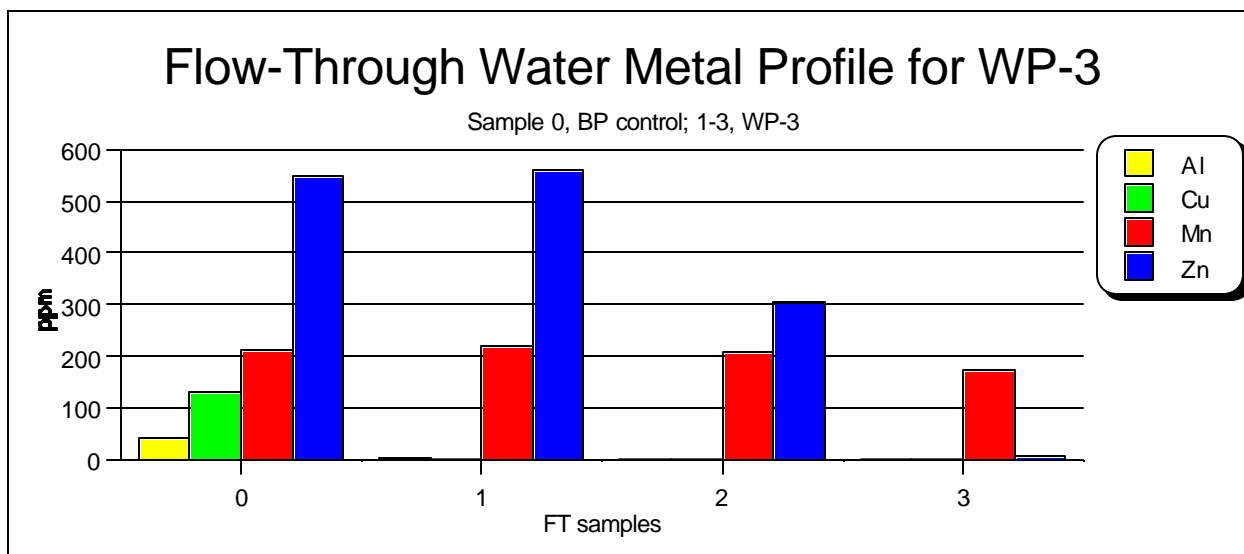


Figure 4-12. Plot of metal ion profile of flow-through water.

5. CONCLUSIONS

The results of this speciation demonstration provide valuable information regarding the use of WP-1, WP-2, and WP-3 to speciate mixtures of metal ions present in Berkeley Pit water into individual metal ions at very high concentrations.

Generally, based on the test data presented in Section 4, WP-1 behaves similarly to WP-3. WP-2 shows a very important and unique feature of low affinity toward Al ion in the presence of Cu ion. The WP-2 also has low affinity toward Mn with or without Cu. Additionally, WP-1, WP-2, and WP-3 all appear to have low affinity in the presence of Zn.

The speciation test required Fe and Al to be removed by oxidizing Fe^{+2} to Fe^{+3} , followed by adding NaOH to precipitate Al and Fe. During the pH adjustment step (see Table 4-1), at a pH of 4.4, most of the Fe was removed by precipitation; however, Al still existed at 195 ppm. As the pH increased, the concentration of Al and Fe decreased, as did the Cu ion concentration, which, is not a desirable trend. After completing the speciation test demonstration, a better understanding of the performance of each chelator gel was realized, and it is determined this precipitation procedure warrants revision.

A possible option for future research would be to adjust the pH to 4.4 to remove most of the Fe, thus allowing the supernatant to pass through WP-2 columns first to concentrate and remove Cu ion while allowing Al, Mn, and Zn ions to flow through the columns. After collecting the column flow-through, the pH of the flow-through would be adjusted to 6 to remove Al, while concentrations of Zn and Mn would remain the same as in the original Berkeley Pit water (see Table 4-4). Retaining most of the Zn and Mn in solution at a pH of 6 is justified based on the data presented in Table 4-1 and Table 4-4 and on the precipitation protocols investigated by Dr. Huang

at Montana Tech. After removing Al, the remaining Zn and Mn ions can easily be separated by WP-1. The manufacturing cost for WP-3 is 23% higher than the cost for WP-1, which is based on the current reagent catalog costs for WP-3. Therefore, it is important to speciate the metal ions in Berkeley Pit water without using the more expensive WP-3.

The volume and strength of the acid used to elute the bound metal ions from the column were not optimized in this demonstration. By reducing the volume and increasing the strength of the acid, it is anticipated that the concentration of the metal ion eluted from the column can be increased significantly.

In conclusion, the speciation test generates better than 93% pure Cu at a concentration of over 2,400 ppm with WP-2 and 95% pure Zn at a concentration of over 2,700 ppm. These values represent a concentration factor of 20 and 5, respectively, without a real attempt at optimization.

Although Mn concentration was not tested, effective concentration can be anticipated by using additional cycles or larger amounts of gel. The onset of Mn concentration can be observed in sample 9 of Table 4-2.

The results obtained from this demonstration clearly warrant further pilot-scale demonstrations. Incorporating the above-suggested changes in the protocol, a pilot-scale speciation and concentration system should be able to be constructed that would operate at 1 to 5 L/min flow rates using WP-2/WP-1 combination columns. Some additional small-scale experiments, namely optimization of elution conditions and the suggested changes in the precipitation procedure, should be performed as part of the scaleup project. From the data gathered to date, it should be possible to calculate column configuration and

dimensions to further optimize speciation, leading directly to a much larger scale system.

In a previous study, it was demonstrated that WP-1 columns can be regenerated more than 2,000 cycles without any appreciable loss in capacity for Cu ion (see Purity Systems' Performance Data Sheet in Appendix C). Taken

together with the results generated from this demonstration, the three most important features of a resource recovery system have been proven with the Purity Systems' materials: concentration of Cu, Zn, and Mn; speciation of Cu, Zn, and Mn; and regeneration of WP-1 columns.

Appendix A

Heavy Metal Ion Extraction Technology

Purity Systems, Inc., has developed a prototypic material for removing heavy metal ions from liquid streams. This technology is based on a silica support, which selectively binds and extracts metal ions that are of concern to and regulated by the U.S. Environmental Protection Agency (EPA). The material has the following characteristics, which are critical to this technology:

- C Extremely high binding affinity for toxic metal ions. It extracts lead (Pb) from water to residual concentrations below 0.002 parts per million (ppm).
- C High metal ion binding capacity allows the use of a small container to extract contaminants from large quantities of water.
- C Unmeasurable leaching of contaminant from support.
- C No breakthrough of contaminant from support.
- C Color changes observed as contaminant is captured in filter material, providing a unique indicator of progressive saturation.
- C Improved effectiveness with multi-contaminant challenge.
- C Easy regeneration of media allows recycling (up to 2,000 cycles at pH extremes).
- C Proprietary surface chemistry with patent application pending.

The Purity Systems' heavy metal ion extraction technology can be used for a variety of applications, including, but not limited to, the following:

- C Point-of-use removal of Pb, copper (Cu), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), and other heavy metal ions from potable water.
- C Water purification for food processing and beverages.
- C Removal of radioactive wastes.

- C Reclamation of in-line wastewater.
- C Removal of concentrations of heavy metals from field water samples.

Purity Systems is soliciting inquiries from parties interested in establishing a joint venture to further develop this material and other technologies. For additional information, fax inquiries to (406) 728-6776, Attention: Dr. Phil Barney.

The stringent regulations imposed by the EPA on industries regarding the content of heavy-metal ions in water discharges have created extensive opportunities in the field of water cleanup. To remove metal ions from polluted water, several factors need to be considered in selecting materials used in cleanup processes:

- C Process speed
- C Degree of removal at process speed
- C Capacity for removal of contaminants
- C Regeneration of extraction material
- C Cost of extraction material - dollar/gallon of water cleaned.

Silica gel columns provide several advantages for this process.

- C Silica gel is rigid and, therefore, can handle high flow rates.
- C The gel can be regenerated very quickly and easily.
- C Surface area per unit of gel is very high with very high capacity.
- C Recycling by regeneration results in low cost per gallon cleaned.

Standard silica gel has an important drawback, i.e., the gel particles start to dissolve at high pH levels. This dissolution will leach the bound metal ions back to the stream and simultaneously reduce the capacity of the system. This leads to a reduced

lifetime for the gel.

Purity Systems has developed a proprietary chemical process that renders the silica gel-based solid support highly resistant to erosion at pH extremes. A series of three different chelators have been covalently coupled to the gel. The chelators are designed to bind only to heavy metal ions, such as Pb and Hg. Useful ions, such as calcium (Ca) and magnesium (Mg) are not bound. When the capacity of the gel is reached, the bound ions can be removed easily, and the gel can be used again. Test results show the gel can be used for thousands of cycles without a significant decrease in flow or capacity. One of the chelator gels will bind toxic heavy metal ions extremely tightly. This gel proved to be excellent for removing toxic metal ions from drinking water without leaching of the bound ions even after prolonged standing.

WP-1

Purity Systems' Water Purification 1 (WP-1) is a silica gel coated with a metal ion capturing matrix using a newly developed technology that renders the material highly resistant to acid and base degradation. The gel size and the pore size were selected to strike an optimal balance between metal ion capacity and diffusion through the gel. The WP-1 provides a high degree of metal ion removal at a rate of throughput one to two orders of magnitude faster than conventional polymer resin products. The functional groups are immobilized covalently onto the silica gel and are unique in that WP-1 can be used to remove either positively charged heavy metal ions or negatively charged oxy-anions simply by changing the operational conditions.

In Figure A-1, deprotonated WP-1 (45 grams (g)) was packed into a column with a diameter of 5 centimeters (cm) and a length of 5 cm. Regular tap water was spiked with Cd ion at 0.150 ppm. This water was pumped through the column at 30 pounds per square inch (psi) and a flow rate of 0.5

Figure A-1. WP-1: Cadmium ion removal.
gallons per minute (gal/min). The Cd concentration of the processed water collected

Figure A-2. WP-1: Chromate removal.

from the outlet was determined by Atomic Absorption (AA), and the results are shown in Figure A-1.

In Figure A-2, 1.0 g of WP-1 was packed into a column with 2.4 milliliters (mL) of volume. Deionized water was spiked with 50 ppm of Cr(VI), as chromate, and the water was pumped through the column at 48 mL/min (or 20 column volumes per minute). The results are shown in Figure A-2.

Field of application: Removal of heavy metal ions in contaminated water, from ppm range to less than 1 ppm and precious metal recovery.

WP-2

Purity Systems' Water Purification 2 (WP-2) is based on the same acid- and base-resistant coated silica gel as the WP-1.

The unique feature of WP-2 is the functional group on the chelator, which is immobilized onto the silica gel. This functional group enables the chelator to bind heavy metal ions more effectively than it binds Ca, Mg, and sodium (Na) ions. Because of this property, WP-2 is used to polish water contaminated with low levels of toxic heavy metal ions, thus reducing the contaminants to an extremely low level and resulting in water that is not toxic according to EPA regulations.

A typical example is the removal of Pb ions in tap water from a concentration of 0.150 ppm* to less than 0.015 ppm. In Figure A-3, WP-2 (45.0 g) was packed into a column with a diameter of 5 cm and a length of 4.5 cm. Tap water spiked with Pb ion to 0.150 ppm was pumped through the column at 30 psi with a flow rate of 0.5 gal/min. The processed water was sampled, and the Pb ion content was determined by AA.

WP-2 allows for multiple regeneration with great

Figure A-3. WP-2: Lead ion removal.

gel stability. In Figure A-4, a column with 2.4 mL of WP-2 was saturated with 50 (mM) of Cu

Figure A-4. Variation in capacity versus number of cycle.

solution followed by acid elution of the bound Cu ion and regeneration with base. After the indicated number of cycles, the capacity of the column was measured, and the results were plotted.

Field of application: Industrial removal of heavy metal ions in continuous processes where multiple recycling of the gel and/or metal ion concentration is desired.

*National Sanitation Foundation recommended challenge level for this metal ion.

Figure A-5. Wp-3: Mercury ion removal

WP-3

Purity Systems' Water Purification 3 (WP-3) uses the same type of silica gel as WP-1 and WP-2 with a different chelator. The special functional groups render the chelator capable of selectively binding heavy metal ions with an extremely high binding constant. Therefore, this material is used in removing very toxic metal ions from the parts per billion (ppb) range to the sub-ppb level.

Removal of Hg ions from 6 ppb* to less than 0.5 ppb** is shown in Figure A-5. Removal of Cd ions from 30 ppb* to less than 0.5 ppb** is shown in Figure A-6. Removal of Pb ions from 150 ppb* to less than 1 ppb** is shown in Figure A-7.

Figure A-6. WP-3: Cadmium ion removal.

For each of the tests, WP-3 (45.0 g) was packed into a column with a diameter of 5.0 cm and a length of 4.5 cm. Tap water spiked with mercury chloride (HgCl_2), cadmium chloride (CdCl_2), or lead chloride (PbCl_2) to the challenged concentrations was pumped through the column at 30 psi with a flow rate of 0.5 gal/min. The processed water was sampled, and the metal ion content was determined by AA. This material offers the advantage of very low leaching rates, relative to WP-2 and WP-1, and excellent stability. The gel has the unique feature of changing color as the metal ion capacity is reached, thus providing an intrinsic indicator of saturation.

Figure A-7. WP-3: Lead ion removal.

Field of application: Point-of-use drinking water metal ion removal.

** Less than 25% of the Maximum Permissible Level (MPL) established in the EPA Primary Drinking Water Regulations.

* National Sanitation Foundation (NSF) recommended challenge levels for these metal ions.

Table A-1. Conversion Table.

WP-1	50 mL/min	Sample	PSI #		FT Sample	PSI #
		1	1		1	55
		2	2		2	56
		3	3		3	57
		4	4			
		5	5			
		6	6			
		7	7			
		8	8			
		9	9			
WP-1	25 mL/min	Sample	PSI #		FT Sample	PSI #
		1	10		1	58
		2	11		2	59
		3	12		3	60
		4	13			
		5	14			
		6	15			
		7	16			
		8	17			
		9	18			
WP-2	50 mL/min	Sample	PSI #		FT Sample	PSI #
		1	19		1	61
		2	20		2	62
		3	21		3	63
		4	22			
		5	23			
		6	24			
		7	25			
		8	26			
		9	27			
WP-2	25 mL/min	Sample	PSI #		FT Sample	PSI #
		1	28		1	64
		2	29		2	65

		3	3		3	57
		3	30		3	66
		4	31			
		5	32			

Table A-1. Conversion table (cont'd).

		7	34			
		8	35			
		9	36			
WP-3	50 mL/min	Sample	PSI #		FT Sample	PSI #
		1	37		1	67
		2	38		2	68
		3	39		3	69
		4	40			
		5	41			
		6	42			
		7	43			
		8	44			
		9	45			
WP-3	25 mL/min	Sample	PSI #		FT Sample	PSI #
		1	46		1	70
		2	47		2	71
		3	48		3	72
		4	49			
		5	50			
		6	51			
		7	52			
		8	53			
		9	54			

Appendix B

Quality Control Section

Frequency of Quality Control (QC) Checks

The quality control (QC) checks were run in accordance with the quality assurance project plan (QAPP). Table B-1 represents the procedure and the frequency of the checks.

RPD: Relative Percent Difference

Calibration

Calibration Levels

The calibration levels used for each standard are represented in Table B-2. All units are in parts per million (ppm).

If calibration was determined to be out of acceptance, the inductively coupled plasma (ICP) was recalibrated. If calibration was not acceptable, the data was flagged in accordance with Laboratory Data Validation Functional Guidelines for Evaluating Inorganic Analyses.

Blanks

The only type of blank used was the calibration blank. This blank was used after instrument, initial, and continuing calibration standards. The calibration blank was reagent grade water acidified to a pH of less than 2 using 2% intra-analyzed nitric acid. The objective of the blank was to determine the existence and magnitude of contamination problems caused by instrument carryover. The calibration blank was used to determine instrument detection limits.

Analytical Duplicates

These samples were used to determine the precision of the analytical method. Precision is calculated from analysis of sample duplicates according to the following equation for ICP and ion chromatographic determinations:

$$RPD = 100 * \{(C1-C2)/[(C1+C2)/2]\}$$

Where:

-
- C1: Larger of the two observed values
C2: Smaller of the two observed values

All duplicates met the acceptance criteria set forth in the QAPP.

Matrix Spikes

A matrix spike was performed on each batch of samples. The spike sample analysis was designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The recovery of matrix spike samples was to calculate the accuracy of the measurement. Accuracy is calculated using the following percent recovery equation. The spiking levels used are provided in Table B-3.

Accuracy—Accuracy is defined as the percent recovery of laboratory matrix spikes. This value will be calculated for ICP and ion chromatographic analysis as follows:

$$\%R = 100 * (S-U)/C$$

Where:

- %R: Percent Recovery
- S: Measured concentration in spiked aliquot
- U: Measured concentration in unspiked aliquot
- C: Actual concentration of spike added

The spike data indicated there were some low and some high spikes. Those matrix spikes that failed the acceptance criteria caused some of the data to be flagged with a J (estimated value). Table B-4 represents the percent recovered for all of the matrix spikes.

Other QC Checks

The following QC checks were run in addition to the previously described checks:

Interference Check Standard—Run at the beginning and end of each analysis run. This is a standard that contains low concentrations of the

target analytes and high concentrations of the interference elements.

Interelement Correction for ICP—Before any samples are analyzed, the ICP Interelement Correction Factor will be determined. Correction factors for aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), and other elements will be determined at all wavelengths used for each analyte reported by the ICP and that cause significant interferences.

ICP Serial Dilution Analysis—A minimum of one analysis per similar matrix type and for each digestion batch will be determined. This analysis monitors the effect of dilution on the original sample concentration. The acceptance criteria for ICP serial dilutions is agreement within + 20%.

Table B-1. QC checks.

Procedure	Frequency
Calibrate instrument	Batch
Analyze calibration standard	Batch
Lab blank	Batch (≤ 20)
Analytical duplicates	Batch (≤ 20)
Check standard	End of run, every 10 samples
Calibration blank	End of run, every 10 samples
Matrix spike	Batch (≤ 20)
Check standard	Batch (≤ 20)

Table B-2. Calibration standards.

Element	Low Standard	High Standard
Al	1	500
Mn	1	500
Cu	1	250
Zn	1	200
Fe	1	500
Fe (II)	1	500

Table B-3. Spike values.

Element	Spike Values (ppm)
Al	4.43
Mn	4.29
Cu	13.29
Zn	14.26
Fe	17.94
Fe (II)	17.94

Table B-4. Percent recoveries of matrix spikes.

Metal	% Recovery Spike #1 MW3-9-96	% Recovery Spike #2 MW3-9-96	% Recovery Spike #1 MW3-11-96	% Recovery Spike #2 MW3-11-96
Al	142	16	-143 Low Spike	105 High Spike
Cu	21.94 Low Spike	75.85 High Spike	-361.4 Low Spike	<MDL

Fe	148.4 High Spike	<MDL	115.86 High Spike	<MDL
Fe (II)	129.2 High Spike	63.96 High Spike	114.4 High Spike	110.8 High Spike
Mn	154.6 High Spike	53.22 High Spike	117.58	98.14 Low Spike
Zn	140.85	-143.6 Low Spike	88.48	92.46 Low Spike

Appendix C

Purity Systems, Inc. Data

PSI Data							
		Raw Data			Within		
Sample	Metal	Concentration	Dillution	Raw Data	Calibration	>MDL	Flag
PSI#2X16	Al	531.1213	16	33.195	Yes	Yes	
	Cu	2369.1042	16	148.069	Yes	Yes	
	Fe	0.6908	16	0.043	0	Yes	J
	Fe (II)	1.1689	16	0.073	0	Yes	J
	Mn	37.4279	16	2.339	Yes	Yes	
	Zn	253.0697	16	15.817	Yes	Yes	
PSI#3X16	Al	433.9592	16	27.122	Yes	Yes	
	Cu	1128.6328	16	70.540	Yes	Yes	
	Fe	0.403	16	0.025	0	Yes	J
	Fe (II)	1.082	16	0.068	0	Yes	J
	Mn	28.1976	16	1.762	Yes	Yes	
	Zn	1355.943	16	84.746	Yes	Yes	
PSI#4X16	Al	4.8416	16	0.303	0	Yes	J
	Cu	12.5249	16	0.783	0	Yes	J
	Fe	0.4073	16	0.025	0	Yes	J
	Fe (II)	1.2092	16	0.076	0	Yes	J
	Mn	41.8035	16	2.613	Yes	Yes	
	Zn	2718.4248	16	169.902	Yes	Yes	
PSI#5X16	Al	10.4594	16	0.654	0	Yes	J
	Cu	4.51	16	0.282	0	Yes	J
	Fe	0.5553	16	0.035	0	Yes	J
	Fe (II)	2.1645	16	0.135	0	Yes	J
	Mn	14.5403	16	0.909	0	Yes	J
	Zn	2769.6523	16	173.103	Yes	Yes	
PSI#6X16	Al	12.8836	16	0.805	0	Yes	J
	Cu	3.1444	16	0.197	0	Yes	J
	Fe	0.6534	16	0.041	0	Yes	J
	Fe (II)	2.8029	16	0.175	0	Yes	J
	Mn	156.9961	16	9.812	Yes	Yes	
	Zn	2772.0903	16	173.256	Yes	Yes	
PSI#7X16	Al	4.9278	16	0.308	0	Yes	J
	Cu	0.5931	16	0.037	0	Yes	J
	Fe	0.5088	16	0.032	0	Yes	J
	Fe (II)	1.8878	16	0.118	0	Yes	J
	Mn	100.3199	16	6.270	Yes	Yes	
	Zn	2773.2244	16	173.327	Yes	Yes	
PSI#8X16	Al	3.0606	16	0.191	0	Yes	J
	Cu	0.5305	16	0.033	0	Yes	J

	Fe	0.7098	16	0.044	0	Yes	J
	Fe (II)	3.6428	16	0.228	0	Yes	J
	Mn	239.2887	16	14.956	Yes	Yes	
	Zn	2773.9651	16	173.373	Yes	Yes	
PSI#9X16	Al	BDL	16	BDL	No	No	
	Cu	BDL	16	BDL	No	No	
	Fe	1.1997	16	0.075	0	Yes	J
	Fe (II)	9.9075	16	0.619	0	Yes	J
	Mn	764.5024	16	47.781	Yes	Yes	
	Zn	1272.9705	16	79.561	Yes	Yes	
PSI#10X16	Al	702.126	16	43.883	Yes	Yes	
	Cu	2668.904	16	166.807	Yes	Yes	
	Fe	1.898	16	0.119	0	Yes	J
	Fe (II)	2.5666	16	0.160	0	Yes	J
	Mn	30.004	16	1.875	Yes	Yes	
	Zn	100.6173	16	6.289	Yes	Yes	
PSI#11X16	Al	548.699	16	34.294	Yes	Yes	
	Cu	2371.8984	16	148.244	Yes	Yes	
	Fe	0.6866	16	0.043	0	Yes	J
	Fe (II)	1.3957	16	0.087	0	Yes	J
	Mn	61.2284	16	3.827	Yes	Yes	
	Zn	160.6674	16	10.042	Yes	Yes	
PSI#12X16	Al	368.4227	16	23.026	Yes	Yes	
	Cu	929.7369	16	58.109	Yes	Yes	
	Fe	0.8716	16	0.054	0	Yes	J
	Fe (II)	1.9417	16	0.121	0	Yes	J
	Mn	83.1658	16	5.198	Yes	Yes	
	Zn	1401.543	16	87.596	Yes	Yes	
PSI#13X16	Al	18.0937	16	1.131	Yes	Yes	
	Cu	16.1797	16	1.011	Yes	Yes	
	Fe	0.5622	16	0.035	0	Yes	J
	Fe (II)	2.153	16	0.135	0	Yes	J
	Mn	112.1905	16	7.012	Yes	Yes	
	Zn	2776.1655	16	173.510	Yes	Yes	
PSI#14X16	Al	12.3738	16	0.773	0	Yes	J
	Cu	5.1816	16	0.324	0	Yes	J
	Fe	0.6432	16	0.040	0	Yes	J
	Fe (II)	3.1621	16	0.198	0	Yes	J
	Mn	166.3435	16	10.396	Yes	Yes	
	Zn	2769.6584	16	173.104	Yes	Yes	
PSI#15X16	Al	10.9618	16	0.685	0	Yes	J
	Cu	2.3709	16	0.148	0	Yes	J
	Fe	0.7556	16	0.047	0	Yes	J
	Fe (II)	3.1514	16	0.197	0	Yes	J
	Mn	189.9569	16	11.872	Yes	Yes	

	Zn	2771.2664	16	173.204	Yes	Yes	
PSI#16X16	Al	4.7511	16	0.297	0	Yes	J
	Cu	0.8345	16	0.052	0	Yes	J
	Fe	0.7763	16	0.049	0	Yes	J
	Fe (II)	3.0829	16	0.193	0	Yes	J
	Mn	194.4055	16	12.150	Yes	Yes	
	Zn	2772.26	16	173.266	Yes	Yes	
PSI#17X16	Al	6.2312	16	0.389	0	Yes	J
	Cu	1.2512	16	0.078	0	Yes	J
	Fe	BDL	16	BDL	No	No	
	Fe (II)	2.0377	16	0.127	0	Yes	J
	Mn	248.23	16	15.514	Yes	Yes	
	Zn	2371.4153	16	148.213	Yes	Yes	
PSI#18X16	Al	4.5593	16	0.285	0	Yes	J
	Cu	BDL	16	BDL	No	No	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	5.1194	16	0.320	0	Yes	J
	Mn	696.7907	16	43.549	Yes	Yes	
	Zn	1472.4939	16	92.031	Yes	Yes	
PSI#19X16	Al	48.0797	16	3.005	Yes	Yes	
	Cu	2462.094	16	153.881	Yes	Yes	
	Fe	0.7706	16	0.048	0	Yes	J
	Fe (II)	1.1202	16	0.070	0	Yes	J
	Mn	4.5217	16	0.283	0	Yes	J
	Zn	110.0533	16	6.878	Yes	Yes	
PSI#20X16	Al	47.1217	16	2.945	Yes	Yes	
	Cu	2213.2222	16	138.326	Yes	Yes	
	Fe	0.3418	16	0.021	0	Yes	J
	Fe (II)	0.7739	16	0.048	0	Yes	J
	Mn	5.6716	16	0.354	0	Yes	J
	Zn	215.7705	16	13.486	Yes	Yes	J
PSI#21X16	Al	86.8138	16	5.426	Yes	Yes	
	Cu	1193.5165	16	74.595	Yes	Yes	
	Fe	0.36	16	0.023	0	Yes	J
	Fe (II)	0.624	16	0.039	0	Yes	J
	Mn	8.9241	16	0.558	0	Yes	J
	Zn	820.723	16	51.295	Yes	Yes	J
PSI#22X16	Al	112.3859	16	7.024	Yes	Yes	
	Cu	139.8287	16	8.739	Yes	Yes	
	Fe	0.3996	16	0.025	0	Yes	J
	Fe (II)	1.1452	16	0.072	0	Yes	J
	Mn	8.0048	16	0.500	0	Yes	J
	Zn	1396.5072	16	87.282	Yes	Yes	J
PSI#23X16	Al	98.9645	16	6.185	Yes	Yes	
	Cu	79.2522	16	4.953	Yes	Yes	

	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.7902	16	0.049	0	Yes	J
	Mn	10.664	16	0.667	0	Yes	J
	Zn	1586.1749	16	99.136	Yes	Yes	J
PSI#24X16	Al	89.2172	16	5.576	Yes	Yes	
	Cu	52.2127	16	3.263	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.6959	16	0.043	0	Yes	J
	Mn	11.8187	16	0.739	0	Yes	J
	Zn	1593.9983	16	99.625	Yes	Yes	J
PSI#25X16	Al	86.8415	16	5.428	Yes	Yes	
	Cu	14.5093	16	0.907	0	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.0469	16	0.065	0	Yes	J
	Mn	11.7169	16	0.732	0	Yes	J
	Zn	1438.8583	16	89.929	Yes	Yes	J
PSI#26X16	Al	71.4403	16	4.465	Yes	Yes	
	Cu	11.906	16	0.744	0	Yes	J
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.663	16	0.041	0	Yes	J
	Mn	16.1379	16	1.009	Yes	Yes	J
	Zn	1508.5654	16	94.285	Yes	Yes	J
PSI#27X16	Al	78.3484	16	4.897	Yes	Yes	
	Cu	10.009	16	0.626	0	Yes	J
	Fe	0.5901	16	0.037	0	Yes	J
	Fe (II)	1.4451	16	0.090	0	Yes	J
	Mn	24.1044	16	1.507	Yes	Yes	
	Zn	1680.1027	16	105.006	Yes	Yes	
PSI#28X16	Al	94.4424	16	5.903	Yes	Yes	
	Cu	2518.7886	16	157.424	Yes	Yes	
	Fe	0.5976	16	0.037	0	Yes	J
	Fe (II)	0.9235	16	0.058	0	Yes	J
	Mn	3.5992	16	0.225	0	Yes	J
	Zn	101.6378	16	6.352	Yes	Yes	
PSI#29X16	Al	51.3597	16	3.210	Yes	Yes	
	Cu	2422.2212	16	151.389	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.7483	16	0.047	0	Yes	J
	Mn	3.0616	16	0.191	0	Yes	J
	Zn	162.7979	16	10.175	Yes	Yes	
PSI#30X16	Al	86.5817	16	5.411	Yes	Yes	
	Cu	1015.3137	16	63.457	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.9265	16	0.058	0	Yes	J
	Mn	5.1833	16	0.324	0	Yes	J

	Zn	920.5148	16	57.532	Yes	Yes	
PSI#31X16	Al	108.7575	16	6.797	Yes	Yes	
	Cu	83.7663	16	5.235	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.5293	16	0.033	0	Yes	J
	Mn	4.1097	16	0.257	0	Yes	J
	Zn	1303.356	16	81.460	Yes	Yes	
PSI#32X16	Al	89.7959	16	5.612	Yes	Yes	
	Cu	66.8312	16	4.177	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.8593	16	0.054	0	Yes	J
	Mn	5.4203	16	0.339	0	Yes	J
	Zn	1481.6877	16	92.605	Yes	Yes	
PSI#33X16	Al	97.9373	16	6.121	Yes	Yes	
	Cu	49.3176	16	3.082	Yes	Yes	
	Fe	0.4934	16	0.031	0	Yes	J
	Fe (II)	1.0512	16	0.066	0	Yes	J
	Mn	7.6819	16	0.480	0	Yes	J
	Zn	1666.1199	16	104.132	Yes	Yes	
PSI#34X16	Al	81.9958	16	5.125	Yes	Yes	
	Cu	8.3949	16	0.525	0	Yes	J
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.5833	16	0.036	0	Yes	J
	Mn	6.7292	16	0.421	0	Yes	J
	Zn	1359.6774	16	84.980	Yes	Yes	
PSI#35X16	Al	60.522	16	3.783	Yes	Yes	
	Cu	9.8473	16	0.615	0	Yes	J
	Fe	0.3775	16	0.024	0	Yes	J
	Fe (II)	0.6394	16	0.040	0	Yes	J
	Mn	8.8207	16	0.551	0	Yes	J
	Zn	1443.3539	16	90.210	Yes	Yes	
PSI#36X16	Al	50.1371	16	3.134	Yes	Yes	
	Cu	7.3191	16	0.457	0	Yes	J
	Fe	BDL	16	BDL	No	No	
	Fe (II)	0.6279	16	0.039	0	Yes	J
	Mn	10.8374	16	0.677	0	Yes	J
	Zn	1437.817	16	89.864	Yes	Yes	
PSI#37X16	Al	613.9784	16	38.374	Yes	Yes	
	Cu	2376.1809	16	148.511	Yes	Yes	
	Fe	1.2072	16	0.075	0	Yes	J
	Fe (II)	1.7026	16	0.106	0	Yes	J
	Mn	10.3284	16	0.646	0	Yes	J
	Zn	149.9705	16	9.373	Yes	Yes	
PSI#38X16	Al	519.1847	16	32.449	Yes	Yes	
	Cu	2053.457	16	128.341	Yes	Yes	

	Fe	1.0371	16	0.065	0	Yes	J
	Fe (II)	1.6842	16	0.105	0	Yes	J
	Mn	16.924	16	1.058	Yes	Yes	
	Zn	289.2982	16	18.081	Yes	Yes	
PSI#39X16	Al	458.7877	16	28.674	Yes	Yes	
	Cu	710.4659	16	44.404	Yes	Yes	
	Fe	0.7389	16	0.046	0	Yes	J
	Fe (II)	1.8276	16	0.114	0	Yes	J
	Mn	27.8054	16	1.738	Yes	Yes	
	Zn	1014.954	16	63.435	Yes	Yes	
PSI#40X16	Al	93.5701	16	5.848	Yes	Yes	
	Cu	272.602	16	17.038	Yes	Yes	
	Fe	0.5628	16	0.035	0	Yes	J
	Fe (II)	1.8705	16	0.117	0	Yes	J
	Mn	62.4435	16	3.903	Yes	Yes	
	Zn	2369.8723	16	148.117	Yes	Yes	
PSI#41X16	Al	11.7274	16	0.733	0	Yes	J
	Cu	130.7298	16	8.171	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.0072	16	0.063	0	Yes	J
	Mn	49.9488	16	3.122	Yes	Yes	
	Zn	2591.0039	16	161.938	Yes	Yes	
PSI#42X16	Al	10.9503	16	0.684	0	Yes	J
	Cu	95.3318	16	5.958	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.1106	16	0.069	0	Yes	J
	Mn	51.8248	16	3.239	Yes	Yes	
	Zn	2724.8977	16	170.306	Yes	Yes	
PSI#43X16	Al	7.3058	16	0.457	0	Yes	J
	Cu	177.5822	16	11.099	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.8316	16	0.114	0	Yes	J
	Mn	107.2983	16	6.706	Yes	Yes	
	Zn	2557.7434	16	159.859	Yes	Yes	
PSI#44X16	Al	6.0269	16	0.377	0	Yes	J
	Cu	146.8815	16	9.180	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.7545	16	0.110	0	Yes	J
	Mn	90.2952	16	5.643	Yes	Yes	
	Zn	1987.3807	16	124.211	Yes	Yes	
PSI#45X16	Al	4.7122	16	0.295	0	Yes	J
	Cu	138.8152	16	8.676	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.8933	16	0.118	0	Yes	J
	Mn	148.0878	16	9.255	Yes	Yes	

	Zn	2191.9692	16	136.998	Yes	Yes	
PSI#46X16	Al	762.1871	16	47.637	Yes	Yes	
	Cu	2508.9451	16	156.809	Yes	Yes	
	Fe	1.9555	16	0.122	0	Yes	J
	Fe (II)	2.3886	16	0.149	0	Yes	J
	Mn	21.7098	16	1.357	Yes	Yes	
	Zn	105.4012	16	6.588	Yes	Yes	
PSI#47X16	Al	572.0499	16	35.753	Yes	Yes	
	Cu	2508.3059	16	156.769	Yes	Yes	
	Fe	0.5133	16	0.032	0	Yes	J
	Fe (II)	1.662	16	0.104	0	Yes	J
	Mn	54.0224	16	3.376	Yes	Yes	
	Zn	155.8728	16	9.742	Yes	Yes	
PSI#48X16	Al	495.7646	16	30.985	Yes	Yes	
	Cu	1387.4385	16	86.715	Yes	Yes	
	Fe	0.8151	16	0.051	0	Yes	J
	Fe (II)	1.7002	16	0.106	0	Yes	J
	Mn	39.9045	16	2.494	Yes	Yes	
	Zn	959.5958	16	59.975	Yes	Yes	
PSI#49X16	Al	29.0613	16	1.816	Yes	Yes	
	Cu	136.0874	16	8.505	Yes	Yes	
	Fe	1.3673	16	0.085	0	Yes	J
	Fe (II)	2.1782	16	0.136	0	Yes	J
	Mn	84.8988	16	5.306	Yes	Yes	
	Zn	2541.6794	16	158.855	Yes	Yes	
PSI#50X16	Al	9.0959	16	0.568	0	Yes	J
	Cu	120.6803	16	7.543	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.6752	16	0.105	0	Yes	J
	Mn	108.288	16	6.768	Yes	Yes	
	Zn	2603.9656	16	162.748	Yes	Yes	
PSI#51X16	Al	9.0413	16	0.565	0	Yes	J
	Cu	106.0599	16	6.629	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.2491	16	0.078	0	Yes	J
	Mn	68.3913	16	4.274	Yes	Yes	
	Zn	2431.8599	16	151.991	Yes	Yes	
PSI#52X16	Al	5.5377	16	0.346	0	Yes	J
	Cu	30.2977	16	1.894	Yes	Yes	
	Fe	0.4801	16	0.030	0	Yes	J
	Fe (II)	2.0428	16	0.128	0	Yes	J
	Mn	118.265	16	7.392	Yes	Yes	
	Zn	2417.5815	16	151.099	Yes	Yes	
PSI#53X16	Al	5.9345	16	0.371	0	Yes	J
	Cu	48.1156	16	3.007	Yes	Yes	

	Fe	BDL	16	BDL	No	No	
	Fe (II)	1.7555	16	0.110	0	Yes	J
	Mn	164.766	16	10.298	Yes	Yes	
	Zn	2353.8445	16	147.115	Yes	Yes	
PSI#54X16	Al	5.758	16	0.360	0	Yes	J
	Cu	86.2034	16	5.388	Yes	Yes	
	Fe	BDL	16	BDL	No	No	
	Fe (II)	2.4415	16	0.153	0	Yes	J
	Mn	251.075	16	15.692	Yes	Yes	
	Zn	1949.0571	16	121.816	Yes	Yes	
PSI#55X4	Al	1.8734	4	0.468	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	1.2969	4	0.324	0	Yes	J
	Mn	202.4557	4	50.614	Yes	Yes	
	Zn	503.8812	4	125.970	Yes	Yes	
PSI#56X4	Al	0.9195	4	0.230	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	1.1286	4	0.282	0	Yes	J
	Mn	192.9568	4	48.239	Yes	Yes	
	Zn	254.0935	4	63.523	Yes	Yes	
PSI#57X4	Al	0.8306	4	0.208	0	Yes	J
	Cu	0.2376	4	0.059	0	Yes	J
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.8788	4	0.220	0	Yes	J
	Mn	152.9989	4	38.250	Yes	Yes	
	Zn	3.4672	4	0.867	0	Yes	J
PSI#58X4	Al	0.8588	4	0.215	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	1.2612	4	0.315	0	Yes	J
	Mn	208.3593	4	52.090	Yes	Yes	
	Zn	534.9373	4	133.734	Yes	Yes	
PSI#59X4	Al	BDL	4	BDL	No	No	
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.9059	4	0.226	0	Yes	J
	Mn	190.5574	4	47.639	Yes	Yes	
	Zn	263.2283	4	65.807	Yes	Yes	
PSI#60X4	Al	BDL	4	BDL	No	No	
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.7534	4	0.188	0	Yes	J
	Mn	142.6361	4	35.659	Yes	Yes	

	Zn	1.3896	4	0.347	0	Yes	J
PSI#61X4	Al	29.1105	4	7.278	Yes	Yes	
	Cu	1.3489	4	0.337	0	Yes	J
	Fe	BDL	4	BDL	No	No	
	Fe (II)	1.2657	4	0.316	0	Yes	J
	Mn	219.764	4	54.941	Yes	Yes	
	Zn	549.6732	4	137.418	Yes	Yes	
PSI#62X4	Al	19.8913	4	4.973	Yes	Yes	
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.964	4	0.241	0	Yes	J
	Mn	212.1235	4	53.031	Yes	Yes	
	Zn	387.5902	4	96.898	Yes	Yes	
PSI#63X4	Al	10.8168	4	2.704	Yes	Yes	
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.9828	4	0.246	0	Yes	J
	Mn	209.444	4	52.361	Yes	Yes	
	Zn	189.7113	4	47.428	Yes	Yes	
PSI#64X4	Al	27.5308	4	6.883	Yes	Yes	
	Cu	0.3329	4	0.083	0	Yes	J
	Fe	BDL	4	BDL	No	No	
	Fe (II)	1.0103	4	0.253	0	Yes	J
	Mn	221.6436	4	55.411	Yes	Yes	
	Zn	545.8885	4	136.472	Yes	Yes	
PSI#65X4	Al	17.0554	4	4.264	Yes	Yes	
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.9151	4	0.229	0	Yes	J
	Mn	214.8597	4	53.715	Yes	Yes	
	Zn	353.8597	4	88.465	Yes	Yes	
PSI#66X4	Al	7.699	4	1.925	Yes	Yes	
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.6587	4	0.165	0	Yes	J
	Mn	205.0425	4	51.261	Yes	Yes	
	Zn	157.9787	4	39.495	Yes	Yes	
PSI#67X4	Al	2.56	4	0.640	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.5818	4	0.145	0	Yes	J
	Mn	214.0046	4	53.501	Yes	Yes	
	Zn	415.9149	4	103.979	Yes	Yes	
PSI#68X4	Al	BDL	4	BDL	No	No	
	Cu	BDL	4	BDL	No	No	

	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.3365	4	0.084	0	Yes	J
	Mn	199.7598	4	49.940	Yes	Yes	
	Zn	218.3791	4	54.595	Yes	Yes	
PSI#69X4	Al	0.8675	4	0.217	0	Yes	J
	Cu	0.1188	4	0.030	0	Yes	J
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.9526	4	0.238	0	Yes	J
	Mn	191.3937	4	47.848	Yes	Yes	
	Zn	15.7061	4	3.927	Yes	Yes	
PSI#70X4	Al	1.554	4	0.389	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.9125	4	0.228	0	Yes	J
	Mn	219.0795	4	54.770	Yes	Yes	
	Zn	560.478	4	140.120	Yes	Yes	
PSI#71X4	Al	0.8896	4	0.222	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.7199	4	0.180	0	Yes	J
	Mn	208.5883	4	52.147	Yes	Yes	
	Zn	304.4906	4	76.123	Yes	Yes	
PSI#72X4	Al	0.7337	4	0.183	0	Yes	J
	Cu	BDL	4	BDL	No	No	
	Fe	BDL	4	BDL	No	No	
	Fe (II)	0.6978	4	0.174	0	Yes	J
	Mn	175.4583	4	43.865	Yes	Yes	
	Zn	6.1008	4	1.525	Yes	Yes	